ANL-6596
Chemical Separations
Processes for
Plutonium and Uranium
(TID-4500, 18th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, September, 1962

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Preceding Quarterly Reports:

- ✓ ANL-6569 April, May, June, 1962
- ANL-6543 January, February, March, 1962
- Ⓒ ANL-6477 October, November, December, 1961

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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SUMMARY

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORTI. Chemical-Metallurgical Processing (pages 29 to 118)

The fifth and final small-scale high-activity-level melt refining experiment has been completed. A 382-g charge of EBR-II prototype fuel (ten percent enriched uranium alloyed with five percent fissionium) irradiated to two total atom percent burnup and cooled 25 days was melt refined for one hour at 1400 C. The yield of purified metal was 73 percent.

An investigation was completed on the behavior of iodine during off-gas-handling operations which follow melt refining of highly irradiated EBR-II fuel. The gases released during melt refining are to be pumped through an iodine trap to an exterior storage tank from which they may be disposed through a stack when meteorological conditions are favorable. It was found that about 10^{-3} percent (an order-of-magnitude value) of the iodine present in the initial charge was removed from the melt refining furnace on pumping it down to a final pressure of 8 mm Hg with the melt refining crucible at a temperature of 650 C. The iodine trap, located between the pump and furnace, consisted of a bed of activated charcoal with AEC filters on the fore and aft sides of the filter to remove particulate activity from the gas stream. The iodine trap removed essentially all of the iodine activity from the gas stream and retained the iodine at the low (8-mm) pressure existing in the final stage of the furnace pumpdown. The effluent from the iodine trap contained of the order of 10^{-6} percent or less of the iodine originally present in the furnace. A small fraction, a few-tenths of a percent, of the rare gas activity in the off-gases was also retained by the charcoal bed.

Four experiments were performed to study the rapid oxidation (mild ignition) of irradiated uranium-fissionium alloy pins in nitrogen-argon atmospheres. (The argon atmosphere in the EBR-II Fuel Cycle Facility may contain as much as five percent nitrogen.) At nitrogen concentrations of five and one hundred percent, the nitridation reaction became self-heating at about 660 C. In one percent nitrogen, self-heating began at about 730 C, and in one-half percent nitrogen, it did not occur on heating the pin to 920 C. At the higher nitrogen concentrations, the ignition temperature may be related to the rapid swelling of irradiated pins, which begins between 600 and 700 C.

The extent of pin nitridation occurring during storage of unirradiated EBR-II fuel pins at 650 C in a five percent nitrogen-argon atmosphere was found to have a negligible effect on melt refining yield (2-kg-scale experiments). The storage conditions employed simulate those expected after

fully irradiated EBR-II fuel pins have been charged to a melt refining crucible, and before the bell jar is sealed and the trapped cell gas is pumped out. Although this result is reassuring, nitridation of irradiated pins could be more extensive than for unirradiated pins, since at 650 C irradiated pins swell (and consequently increase in surface area) due to the pressure of trapped fission gases.

The skull reclamation process is under development for the recovery of skull material which remains in a crucible after melt refining. In the first series of demonstration runs in a recently completed glove box containing an inert atmosphere, difficulty was encountered in the noble metal-extraction step, with only 17 percent of the ruthenium and 54 percent of the molybdenum extracted. Since this difficulty had not previously been encountered in runs in which the halide salts had been exposed to air (thereby allowing absorption of water vapor), the difficulty experienced when the flux is handled in argon may be associated with the elimination of oxygen or water reactions (which produce chlorine and hydrogen chloride gases). In one run the extraction of ruthenium was increased to 63 percent by the presence of zinc chloride in the flux. Other than the difficulty in the noble metal-extraction step, process and equipment performances have been good.

Construction of large-scale integrated equipment (approximately one-half plant scale) for the skull reclamation process has begun. The performance of a prototype transfer tube, fabricated from a 30 weight percent tungsten-molybdenum alloy and used for transfer of molten salt and metal systems by pressure siphoning, was found to be highly satisfactory. The use of simple stainless steel waste containers for waste metal was shown to be feasible.

Development work has continued on separation processes for the fast reactor fuel composed of 20 percent plutonium, 70 percent uranium, and 10 percent fission. One separation procedure under investigation involves an equilibration of the fuel constituents between liquid zinc-magnesium alloys and molten magnesium chloride. Distribution data were reported previously for yttrium, cerium, praseodymium, neodymium, uranium, plutonium, and americium (see ANL-6569, page 39). Distribution data for thorium, vanadium, barium, and zirconium at 800 C between liquid zinc-magnesium and molten magnesium chloride have since been obtained. Thorium, vanadium, and zirconium tend to favor the metal phase, whereas barium appears only in the flux. The effect of uranium concentration on its distribution between magnesium chloride and 10 weight percent magnesium-zinc at 800 C was investigated. The distribution coefficient, $(w/o \text{ in flux} / w/o \text{ in metal})$, for uranium was found to increase as the uranium concentration in the metal phase increased to about two weight percent. Above two weight percent uranium, the distribution coefficient increased only slightly. For an identical metal-salt system, the distribution coefficient for plutonium increased only slightly as the plutonium concentration

in the metal phase was increased from 0.5 weight percent to 4.8 weight percent. The effect on plutonium-praseodymium separation of varying the temperature of a zinc-50 weight percent magnesium, equimolar magnesium chloride-lithium chloride system was investigated. The logarithm of the praseodymium-plutonium separation factor increased linearly as a function of the reciprocal absolute temperature. At 850 C, the praseodymium-plutonium separation factor was 25 and at 620 C it was 47. When the magnesium chloride flux was diluted with lithium chloride in a 800 C system having a zinc-50 weight percent magnesium metal phase, the distribution coefficients for plutonium and praseodymium both decreased gradually at first as the magnesium chloride level was lowered, then dropped off sharply as the magnesium chloride concentration was reduced below about 30 mole percent. Substitution of a cadmium-magnesium metal phase for a zinc-magnesium metal phase in a system at 650 C having a magnesium chloride-50 mole percent lithium chloride flux had little effect on the distribution coefficients of plutonium and praseodymium. Codistribution behavior of uranium, plutonium, and praseodymium between magnesium-zinc solution and molten magnesium chloride at 800 C was identical with the behavior of these elements when present alone in the same system at the same temperature.

Work was continued on the EBR-II blanket process, in which plutonium is separated from uranium by utilizing the high solubility of plutonium in magnesium-rich solutions and the contrasting low solubility of uranium in such solutions. Results of the fifth of a series of blanket runs confirm the general findings of previous runs, namely, good separation of plutonium from uranium (from a plutonium-to-uranium ratio of 1 to 99 in the blanket material to one of about 70 to 30 in plutonium product solution) and potentially high recovery of plutonium (greater than 95 percent).

Tungsten and certain tungsten alloys are among the promising materials for containment of flux and metal systems of the skull reclamation process. Little or no corrosion of tungsten occurred (1) on exposure of tungsten specimens to conditions of the noble metal-extraction step of the skull reclamation process for periods of 400 and 500 hr, and (2) on successive 500-hr exposures of a pressed and sintered tungsten crucible to conditions of the noble metal-extraction and skull oxide-reduction steps.

Molybdenum-30 percent tungsten alloy specimens did not change dimensionally but lost about four percent in weight when exposed to the conditions of item (1) above. An agitator of this alloy was attacked by pitting when used in the tests with the tungsten crucible [item (2) above]. The attack was not severe enough to eliminate consideration of this alloy. Both tungsten and the molybdenum-tungsten alloy are being recommended as construction materials for the skull reclamation process.

Thixotropically cast beryllia crucibles continue to show excellent performance as containers for the last three steps of the skull reclamation

process (two uranium-precipitation steps and a retorting step). No significant change could be detected in two such crucibles, one of which was jacketed in a stainless steel secondary and one of which was unjacketed, after each had been exposed to process systems for about 180 hr. During this time, the systems were thermally cycled ten to twenty times between 450 C and 800 C. Work is beginning on the development of fabrication methods and materials for large-size ceramic containers.

The effect of flux composition on the reduction of thorium dioxide by zinc-magnesium alloy has been redefined, with the use of an argon atmosphere instead of an air atmosphere. The range of flux composition in which satisfactory reduction takes place with calcium chloride-magnesium chloride-calcium fluoride fluxes is greatly increased by the use of the inert atmosphere. At the optimum fluoride anion concentration of 10 atom percent with sufficient thorium dioxide present to give a one percent alloy, only 10 or 11 atom percent magnesium cation is needed to achieve complete reduction of thorium dioxide. A study of other variables involved in the reduction reaction shows that mixing speeds greater than 700 rpm are required for the scale and configuration of the laboratory equipment used, and that the reduction rate increases as the temperature is raised.

Operation of a large cadmium-distillation unit was continued to gain experience on an engineering scale with the distillation operation and associated liquid-metal-handling operations. In recent runs, the uncooled, copper induction coil which introduces power for cadmium vaporization has overheated. This overheating was attributed to reduced emissivity of the coil when decomposition of a copper oxide coating on the coil left a shiny metal surface. An appreciable reduction of coil-operating temperature was effected by coating the coil with aluminum oxide, thereby increasing its emissivity.

A study of the nature of liquid metal boiling and the associated mechanisms of entrainment is underway. A fast-response liquid metal thermocouple system was used to follow rapid temperature fluctuations in boiling liquid metals. Surprisingly large, random temperature fluctuations (nearly 50 C) have been observed, by means of a cathode ray oscilloscope, during surface vaporization (nonturbulent vaporization) of mercury. Under nonturbulent conditions, vaporization rates equivalent to an energy dissipation of about 100,000 Btu/(hr)(sq ft of surface) have been obtained.

Equipment has been constructed by which accurate measurements of mixing power inputs into liquids are possible. Some mixing power data for mercury and for water are reported.

The diffusivity of uranium in liquid bismuth at 725 C was found to range from 2.5×10^{-5} sq cm/sec at 500 C to 4.6×10^{-5} sq cm/sec, with estimated accuracies of ± 15 percent.

The construction of the Fuel Cycle Facility is essentially complete. The work this quarter was largely the determination and correction of deficiencies in construction and vendor-fabricated items.

Operation of the process cell cranes and manipulators revealed extensive difficulties. Discussions are being held with respective manufacturers to determine the proper corrective actions.

All of the windows in the Air and Argon Cells have been installed.

One melt refining furnace and an associated ingot-removal-and-sampling device have been installed in the Argon Cell by the Fuel Cycle Facility operating personnel, with the use of the cell cranes and manipulators. About 90 percent of the equipment in the subcell has been installed and is being tested.

Installation of the transfer lock equipment is continuing.

All 65 service sleeve feed-throughs have been installed in the Argon Cell floor. The installations were found to be leak tight.

One of the two 20-ton coffins to be used to transfer fuel subassemblies between the reactor and the Fuel Cycle Facility is scheduled for delivery in September 1962, and the design of the other is nearly complete. A system has been determined for the in situ removal of sodium from subassemblies in the transfer coffin. The design of a sodium-removal station incorporating this system has begun.

In a study of mercury vapor lamps, the effect of lamp life, operating voltage, and ambient temperature upon the effective illumination in the Argon Cell was predicted, with the use of data obtained from two lamp installations - one in the Senior Cave and one in the Argon Cell mockup. These predictions indicate that the three variables will not cause a serious decrease in the effective illumination in the Argon Cell.

Equipment is being developed to oxidize the skull resulting from the melt refining operation. The oxidation furnace and associated equipment are being assembled as an operating unit for testing. A mechanism is being developed to dump the oxide from the container in which oxidation occurs into a storage container.

Experiments to develop a satisfactory metal vapor condenser for use with the melt refining furnace are continuing. A graphite condenser has been tested and found promising; however, the gasket material used in the test was unsatisfactory. Alternate gasket materials will be tested.

Low-frequency inductive heating and mixing of molten metal and salts is being investigated for use in the skull reclamation process. Results of the tests are promising. In one run with skull oxide a reduction of 40 percent was accomplished, and visual observations indicated vigorous agitation in this and other runs. A gas clean-up system used in these tests greatly decreased the amount of metal or salt fumes and deposits in the furnace during operation.

Fundamental studies of the chemistry of liquid metal systems are being made in connection with the Chemical Engineering Division's work in the field of pyrometallurgical fuel reprocessing. Basic to these practical processes is knowledge of the solubilities of fission product, fissionable, and structural elements in metallic solvents. The solubility of strontium in liquid zinc has been measured. The solubility may be represented by the empirical equation

$$(506 \text{ to } 727 \text{ C}) \text{ Strontium: } \log (\text{atom percent}) = 9.619 - 9940 T^{-1} .$$

The solubilities of zirconium in liquid 20 weight percent magnesium-zinc and in liquid 30 weight percent magnesium-zinc have been measured as a function of temperature. In 20 weight percent magnesium-zinc solutions the solubility varies from 1.6 weight percent at 757 C to 0.02 weight percent at 584 C. A sharp break in the solubility curve occurs at about 630 C suggesting different equilibrium solid phases above and below this temperature. In 30 weight percent magnesium-zinc, the solubility varies from 0.9 weight percent at 764 C to 0.002 weight percent at 482 C. A sharp break in the solubility curve occurs at about 650 C.

The phase diagram for the vanadium-zinc system is presented.

The peritectic temperature for the transformation of the epsilon uranium-zinc intermetallic phase to the delta phase has been established at about 790 C by a combination of solubility studies and thermal analysis studies.

The lanthanum-zinc system has been studied by both the continuous weighing effusion method and by X-ray examination. The following intermetallic phases were found by the effusion method: LaZn_{13} , LaZn_{11} , $\text{La}_2\text{Zn}_{17}$, LaZn_7 , $\text{LaZn}_{5.3}$, LaZn_4 , LaZn_2 , and LaZn .

The magnetic susceptibility of the intermetallic compound UCd_{11} has been remeasured. From 4.2 K to room temperature the susceptibility follows a Curie-Weiss law, $\chi = C/(T - \Delta)$, with $C = 1.77_8$ and $\Delta = -41.2$ K. Below 4.2 K the susceptibility is constant. The data are interpreted on the basis of a $5f^2$ configuration for the uranium atoms perturbed by a nonspherically symmetric electric field.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 119 to 163)

A mixture of uranium hexafluoride and plutonium hexafluoride will be produced by the fluorination of uranium dioxide nuclear fuel in the Direct Fluorination Volatility Process. Plutonium hexafluoride is much less stable than uranium hexafluoride; therefore, thermal decomposition can be used to separate the components of the mixture. Additional experiments have been carried out which have yielded information on both the efficiency and the rate of separation obtained by thermal decomposition. The best separation was obtained at 200 C when a mixture with an initial ratio of uranium to plutonium of 12.8 was circulated through the vessel for 10 hr (this was equivalent to a residence time in the decomposition vessel of 6.6 min for the entire mixture). The ratio increased to 1.94×10^4 , indicating a removal of 99.9 percent of the initial plutonium from the gas. At 300 C, the maximum ratio of uranium to plutonium was reached much more rapidly. During a circulation time of $1\frac{1}{3}$ hr (residence time, 0.88 min) through a vessel at 300 C, the uranium-to-plutonium ratio of a gas mixture was increased from 9.88 to 3.48×10^3 , indicating a removal of 99.7 percent of the initial plutonium from the gas.

The percentage of uranium in the deposited plutonium tetrafluoride increased with the total circulation time (or residence time of the total gas mixture in the hot vessel) for the set of experiments at 300 C. The purest plutonium tetrafluoride product was obtained when a gas mixture with an initial concentration of 90.8 percent uranium hexafluoride in total hexafluorides was circulated through a vessel for $1\frac{1}{3}$ hr (residence time of total mixture, 0.88 min) to deposit plutonium tetrafluoride with a uranium content of 0.091 percent.

It is concluded that thermal decomposition can be used to separate plutonium hexafluoride from uranium hexafluoride between 200 and 300 C at rates which are practical for application to the fluoride volatility processing of power reactor fuels.

An investigation was made of the factors affecting the vapor-phase hydrolysis of plutonium hexafluoride and the filtration of plutonium particulate matter obtained from the hydrolysis. The filters evaluated were AEC-type filters used in glove-box installations at Argonne National Laboratory. Particle-penetration data were obtained from experiments in which small-scale controlled releases of plutonium hexafluoride, 25 mg or less, were made into an atmosphere of known moisture content. The resulting air mixtures were passed through AEC filters, a water bubbler, and Millipore filters in series, at a controlled flow rate. Gamma and/or alpha counts of the filters and bubbler were used to determine penetration for individual and combinations of filters.

The amount of plutonium hexafluoride released varied between 1.5 and 25 mg. The partial pressure of water in the air used varied between 0.77 and 10.64 mm Hg. The air velocity through the filters was 1.0 cm/sec in all experiments. When there was sufficient moisture in the air to hydrolyze completely the plutonium hexafluoride released, the penetration of two AEC filters in series varied from one ppm to two ppb. It has been concluded, upon extrapolation of the information obtained from these experiments, that the Argonne glove-box installations can safely handle up to 50 g of plutonium hexafluoride when the partial pressure of the water in the air used is in excess of 6.8 mm Hg.

The sizes of particles produced by the vapor-phase hydrolysis of plutonium hexafluoride are being determined by examination with an electron microscope. Samples of the material have been collected by an electrostatic precipitator and by AEC filter media. Most of the hydrolyzed plutonium hexafluoride was found in the form of agglomerates, which were found to have a wide size range and were composed of spherical particles from 0.01 to 0.2 μ in diameter.

A study of the decomposition of plutonium hexafluoride 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 plutonium hexafluoride. Data obtained showed an increase of the extent of decomposition with increasing amounts of energy absorbed in plutonium hexafluoride. Plutonium tetrafluoride and fluorine were identified as the products of the decomposition. The G value for the decomposition is 7 molecules of plutonium hexafluoride decomposed per 100 ev absorbed.

The rate of decomposition of plutonium hexafluoride by alpha radiation has been calculated for spherical vessels of 3.175-cm radius with the use of the G value for the decomposition of plutonium hexafluoride by gamma radiation. The calculated values have been compared with the literature values of experimentally determined decomposition rates.

Plutonium hexafluoride has been synthesized by the action of gamma radiation on mixtures of plutonium tetrafluoride and elemental fluorine. The product was identified by its infrared spectrum and its vapor pressure. The quantities of plutonium hexafluoride produced were greater than those expected from the thermodynamic equilibrium constant.

Development has continued of the Direct Fluorination Process applied to uranium dioxide fuel. In this process the uranium and plutonium dioxides from discharged reactor fuel are reacted with fluorine directly to produce hexafluoride products, which are then decontaminated by volatility techniques. Engineering-scale studies thus far have been directed toward process optimization of the primary fluorination of uranium dioxide pellets. The system

used in the studies consists of pellets (or pellet fragments), which form a packed bed, with fluidization of inert solid (alumina grain) being provided in the space above and in the voids of the pellet bed. The fluidization aids in the heat transfer and in the mixing of solid fines formed as intermediates or residues in the system. Oxygen influences the reaction behavior by the formation of uranous oxide (U_3O_8) fines.

In the present period, several runs with 6-in.-deep pellet beds were carried out at 500 C with continuous pellet additions to maintain constant bed height and to approximate steady-state conditions more closely. In one set of runs (without oxygen), the total gas rate was varied in the range of 0.5 to 1.3 ft/sec and resulted in a 40 percent increase in the uranium hexafluoride production rate. In another set of runs, oxygen concentrations of 5 and 13 percent were investigated. Satisfactory fluidization quality was achieved in the run with the lower oxygen concentration, but not in the run with the higher concentration. At 5 percent oxygen, the steady-state production rate was 40 lb uranium hexafluoride/(hr)(sq ft of reactor cross section), and the fluorine utilization efficiency was 56 percent.

An analysis was made of factors having a tendency to produce caking, and, on the basis of this analysis, a two-zone scheme was proposed for study. In this scheme, a mixture of oxygen and nitrogen is introduced into the lower zone, which consists of a uranium dioxide pellet bed, and fluorine is introduced into the upper zone, which consists of a bed of Alundum grain. The Alundum, which also fills the voids of the pellet bed, is fluidized by the mixture of oxygen and nitrogen. This mixture is introduced into the system at the bottom of the pellet zone, while the fluorine is introduced at the bottom of the upper zone, just above the uranium dioxide pellets. Uranium oxide fines (U_3O_8) are formed in the lower zone and elutriated into the upper zone, where they are removed by fluorination. One advantage of this scheme is that the possibility of caking due to reactions of uranium hexafluoride with uranium oxides, which leads to the formation of solids, may be minimized. Another anticipated advantage is that the quality of fluidization in the upper zone will be improved by the absence of uranium dioxide pellets. Also, in the two-zone scheme, heat removal is more favorable than in the one-zone scheme. This arises from the fact that only the oxidation reaction (for which $\Delta H = -26$ kcal/gram.mole uranium at 25 C) takes place in the pellet bed, and fluorination of the fines (for which $\Delta H = -231$ kcal/gram mole uranium at 25 C) takes place in the upper unhindered fluidized bed of Alundum. This more favorable heat condition should minimize the possibility of sintering and should reduce caking. In an initial batch run carried out with a 12-in. pellet bed at 500 C, good fluidization quality was achieved. The gas rate in the pellet zone was 1.2 ft/sec and the oxygen concentration of the gas was 4 to 8 percent. Fluorine concentration in the gas in the upper zone was varied from 5 to 13 percent. The overall uranium hexafluoride production rate was 33 lb uranium hexafluoride/(hr)(sq ft) and overall fluorine utilization efficiency was 61 percent. A review and analysis of runs to date showed several promising methods of pellet fluorination.

A high-alpha facility is being installed for pilot plant-scale studies of the Direct Fluorination Process applied to uranium-plutonium oxide reactor fuels.

Development work on a fluidization-volatility process scheme for the recovery of enriched uranium from low uranium-zirconium alloy fuels is in progress. This process involves a chlorination of the alloy while submerged in an inert fluidized bed and a subsequent fluorination step. The zirconium is separated from the alloy as the volatile tetrachloride during the chlorination step. The uranium is recovered as the volatile hexafluoride during the fluorination step.

In current experiments, the effect on overall uranium recovery of several chlorination-fluorination cycles was studied. One sequence employed hydrogen chloride followed by phosgene and then fluorine. The other employed a 4:1 mixture of hydrogen chloride and phosgene followed by phosgene and fluorine. Previously, only hydrogen chloride and fluorine were used.

Preliminary results on the loss of uranium through the static filter bed during the chlorination step indicate that greater losses were sustained when a hydrogen chloride-phosgene mixture was employed than with hydrogen chloride alone, typical values being 5.0 and 0.2 percent, respectively. In these cases the entire system, both the fluidized bed and static bed, was maintained at a uniform temperature (~400 C). For the chlorination-fluorination cycle it was found that, where the cycle included the mixed reactants, less time and less reactants were needed to reach a given level of uranium retention in the inert solids than when the cycle included separate reactants. Exemplifying the former was an overall cycle time of 9.7 hr with 8 times the stoichiometric chlorinating requirements (based on the initial alloy charge), and an example of the latter was a 19.2-hr cycle and 11 times the chlorinating requirements. The uranium concentrations in the final bed for these two examples were 0.04 and 0.05 weight percent, respectively, corresponding to about 1.0 and 1.3 percent of the initial uranium charge.

A comparison of the data from experiments conducted with both Type 38 Alundum and Type RR Alundum indicates that following an initial fluorination period at 400 C with a short fluorination period at 500 C gives increased uranium removal from the inert solids. In the final beds, residual uranium values of 0.02 and <0.01 weight percent were achieved for the two materials, respectively. Under the conditions noted above, caking of Type 38 Alundum in the filter bed was noted. Also, it appears to undergo attrition more readily during fluidization than Type RR Alundum and thus appears to be less satisfactory as a starting bed material.

Two methods of analysis (infrared spectrophotometric and wet chemical methods) were used in an effort to identify materials which might be associated with the ignitions which occurred after the fluorination step had been completed and the cold traps used for the collection of uranium

hexafluoride were being vented. The traps are normally maintained at about -80°C with a dry ice-trichloroethylene bath. These ignitions have occurred during the current work only when a phosgene-hydrogen chloride mixture was used as the initial reactant. Infrared spectrophotometric analysis of vapor samples taken from each of the three coil-type traps used in series indicated the presence of chlorine trifluoride, chlorine dioxide, and an unidentified compound in the region of 535 to 560 cm^{-1} . Of possible significance is the fact that chemical analysis of the trapped material, following uranium hexafluoride hydrolysis, showed a great excess of fluoride in the material obtained from a run in which a hydrogen chloride-phosgene mixture was used as the initial reactant. This excess was considerably greater than that associated with the material in the traps obtained in runs in which hydrogen chloride alone was used as the initial reactant. Work is being directed towards the elimination of chlorine (possibly by a hydrogen fluoride treatment) before fluorination when the cold traps must be used.

Studies were continued on a fluid-bed-pyrohydrolysis reaction scheme for the disposal of the waste zirconium tetrachloride produced during chlorination of uranium-zirconium alloy fuels. Efforts are directed toward finding operating conditions which will promote efficient deposition of the product (zirconium dioxide) on the inert bed particles and allow operation for extended times. Runs were made in the 6-in.-diameter column at zirconium tetrachloride feed rates ranging from 1.8 to 3.3 kg/hr and steam rates of 2.1 to 5.3 times the stoichiometric requirement. Results were evaluated on the basis of the fraction of fines (-200 mesh material) found in the final bed. Fines produced by attrition alone (a 6-hr run with no tetrachloride feed) represented about five percent of the bed. A lower temperature (currently 250 to 350°C) may also result in more fines. In the other runs, the quantity of fines ranged from 7 to 28 percent in runs of 2.5 - to 6.0 -hr duration. The use of higher filter blowback pressure (80 psig as compared with 30 psig) continues to give satisfactory results with respect to preventing the buildup of fines (and the associated high pressure drop) on the filters.

Exploratory studies of an alternative scheme to process the zirconium tetrachloride off-gas were conducted with static beds of rock salt to absorb the tetrachloride. In one run, made at bed temperatures of 250 to 320°C , a 98 percent absorption of the tetrachloride was achieved with a relatively dilute gas feed (~ 1.4 volume percent tetrachloride in nitrogen). Less satisfactory results were obtained in runs at higher temperatures.

Process development studies on a fluid-bed scheme for preparing high-density spheroidal uranium dioxide particles were continued in a 3-in.-diameter Monel column. The scheme involves vapor-deposition techniques with the system steam-hydrogen-uranium hexafluoride and a starting bed of product uranium dioxide. Current studies using about 6-kg beds (~ 8 -in. static bed height) and the established procedure of a hexafluoride reaction period followed by a residual fluoride cleanup period (steam and hydrogen only) showed the following effects on particle density:

(1) Higher temperatures, 700 C as compared with 650 C, produced a material of higher density, 9.7 to 9.8 g/cc (nearly 90 percent of theoretical).

(2) Decrease of the uranium hexafluoride feed rate from 34 to 17 g/min resulted in the particle density being increased from 9.1 to 9.5 g/cc in two runs.

(3) Low steam rates (below stoichiometric requirements - in one case, no steam feed) during uranium hexafluoride feed periods gave lower densities than high steam rates.

(4) Hexafluoride nozzle position (depth of penetration into the bed) affected density; a long nozzle (extending about $3\frac{3}{4}$ in. vertically upward into the bed) gave material of higher density than a short nozzle (extending $\frac{3}{4}$ in. into the bed).

The length of hexafluoride on-time (15 to 30 min) had no apparent effect on density.

Measurement of distribution of pore size of the uranium dioxide product particles showed most of the pores to be less than $0.4\ \mu$ in diameter and a significant portion to be below $0.06\ \mu$ in diameter. Sintering of dioxide particles in a hydrogen atmosphere for about $2\frac{1}{2}$ hr at temperatures in the range from 1600 to 1725 C gave final particle densities ranging from 10.4 to 10.6 g/cc, or about 95 to 96.5 percent of theoretical density.

The studies investigating the use of small-diameter fluid-bed columns in conjunction with the preparation of nuclear critical materials have been indefinitely suspended because of increased manpower needs in other divisional programs. The $2\frac{1}{4}$ -in.-diameter column and associated equipment have been left in a standby condition.

III. Calorimetry (pages 164 to 174)

Results are reported for a series of combustions of both zirconium dihydride and zirconium dideuteride, carried out on samples of higher purity and better-defined composition than were used in previous Argonne studies of these compounds. New values obtained for the standard enthalpy of formation, ΔH_{298}° , are -38.90 ± 0.31 kcal/mole and -40.25 ± 0.27 kcal/mole for zirconium dihydride and zirconium deuteride, respectively.

Revised data are reported for combustions of magnesium and cadmium in fluorine. The data for magnesium include results of 12 acceptable runs. The new values obtained for the standard enthalpy of formation, ΔH_{298}° , are -264.4 ± 0.6 and -167.5 ± 0.2 kcal/mole for the difluorides of magnesium and cadmium, respectively.

The techniques which were used for combustions of magnesium and cadmium are being used with minor modifications for combustions of aluminum and zinc in fluorine. Experimental work with aluminum is complete, and calorimetric measurements with zinc are in progress.

Calorimetric combustions of uranium in fluorine have been resumed. Preliminary estimates of the results of four experiments indicate that the value for the enthalpy of formation of uranium hexafluoride gas will fall within the range previously reported, -509 ± 3 kcal/mole, but with an uncertainty smaller by approximately an order of magnitude.

Techniques for the determination of the enthalpy of formation of zirconium diboride have been developed, and calorimetric measurements have been started.

IV. Reactor Safety (pages 175 to 200)

The oxidation, ignition, and combustion processes of metals and compounds used in nuclear technology are being studied to provide information to aid in minimizing the hazards associated with handling these materials.

The program of theoretical studies designed to relate ignition results with isothermal oxidation data is continuing. Isothermal oxidation rates of a series of aluminum-uranium alloys [15 to 1130 ppm (1 a/o)] have been determined at 500 C. With increasing aluminum content, oxidation rates were found to increase regularly from decelerating rates, which are characteristic of unalloyed uranium at 500 C, to the accelerating rate previously reported for the 1 atom percent aluminum-uranium alloy. Burning curve ignition experiments had been performed on the same series of aluminum-uranium alloys. Each sample was heated at a uniform rate (usually 10 degrees/min) in a flowing oxidizing atmosphere. The ignition temperature was determined by graphical means from a plot which indicated when the sample began to self-heat (see ANL-5974, page 13, for method of determining ignition temperature). In contrast with the rather uniform increase in oxidation rate at 500 C as aluminum content was increased from 15 ppm to 1130 ppm in the isothermal oxidation study, increasing the aluminum content above about 75 ppm resulted in a lowering of the ignition temperature from 575 to 420 C. It was concluded that increasing the concentration of aluminum in the alloy progressively inhibits the transition at 450 C from an accelerating rate to a decelerating rate. This transition probably represents the formation of a protective oxide film (see ANL-6543, page 168). In alloys containing about 75 ppm aluminum or more, the transition is sufficiently inhibited so that ignition can occur at temperatures below 450 C.

Results of temperature-time burning curve studies with 70 binary uranium alloys have been reviewed and interpreted in the light of the results of recent determinations of isothermal oxidation rates. The temperature-time plots for these binary alloys are varied and complex, but reproducible. Differences in the shapes of the burning curves between unalloyed uranium and uranium alloys have been interpreted in terms of two effects which can occur singly or in combination. One of these is the effect, produced notably by aluminum (but also by certain alloys of beryllium, bismuth, carbon, lead, molybdenum, niobium, palladium, platinum, ruthenium, silicon, titanium, and vanadium), of inhibiting the transition from an accelerating rate to a decelerating rate or increasing the temperature at which the transition occurs, and thereby lowering the ignition temperature. The other effect, produced notably by copper (but also by bismuth, lead, palladium, platinum, ruthenium, and vanadium), is an increased protectiveness of the oxide formed at high temperature. Alloying additions of cerium, chromium, hydrogen, iron, nickel, rhodium, silver, tantalum, thorium, and zirconium had no significant effect on the ignition behavior of uranium.

Additional studies were made of the effect of halogenated hydrocarbons on burning curve ignition temperatures, burning propagation velocities, and maximum burning temperatures of uranium. The addition of two or four volume percent dibromotetrafluoroethane (Freon 114B2) to air has been found to reduce markedly the burning propagation velocity and maximum burning temperature of 0.013×0.3 -cm uranium foil and to inhibit completely propagation in 0.002×0.3 -cm zirconium foil. The burning curve ignition temperature of the uranium foil was lowered from 380 C in air to 320 C in air containing two volume percent of this compound. Freon 114B2 seems to be an attractive agent for use in metal fire protection.

Studies of the ignition of irradiated uranium have been initiated. Small uranium pins will be enclosed in constraint jackets and irradiated in MTR. Sample temperatures during irradiation will be limited to 300 C. It is anticipated that this procedure will minimize surface roughening, directional growth, and swelling.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. One method being used involves the rapid melting and dispersion of metal wires in a water environment by a surge current from a bank of condensers. A series of runs with stainless steel-316 wires in heated water has been completed and compared with previous results in room-temperature water (see ANL-6543, page 182). The amount of metal-water reaction for runs made in water at 100 C (and 15 psia pressure) and in water at 200 C (and 225 psia pressure) did not differ significantly. The runs in heated water had greater metal-water reaction, however, than similar runs in room-temperature water. These results were consistent with previous results reported for the zirconium-water reaction and the uranium-water reaction. A computer

program has been prepared for use with the IBM-704 computer to complete the analysis of uranium-water data and stainless steel-water data obtained by the condenser-discharge method and the in-pile studies in TREAT.

Another method of studying metal-water reactions has been called the volumetric method. In these studies, steam is passed over inductively heated one-cm cubes of the metal under study. Hydrogen generated by metal-water reaction is collected over water and the quantity is measured continuously. Studies were made of the reaction of steam with uranium and with two uranium alloys, one containing 105 ppm aluminum and another containing 1130 ppm aluminum (1 a/o). The presence of aluminum increased the linear-parabolic transition temperature from between 400 and 500 C for unalloyed uranium to about 500 C for the aluminum alloys. Neither the linear rate constant at 400 C nor the parabolic rate constants between 600 and 1200 C were significantly affected by the presence of aluminum. The results showed that the presence of minor quantities of aluminum does not have the striking effect on the uranium-steam reaction that it does on the uranium-oxygen reaction (see page 13).

Studies of metal-water reactions initiated by a nuclear transient are continuing. In these studies, small fuel pins were submerged in water in high-pressure autoclaves which were placed in the center of TREAT and subjected to severe nuclear transients. In-pile studies of Zircaloy-2-clad, 93.5 weight percent uranium, 5 weight percent zirconium, 1.5 weight percent niobium pins were conducted with the autoclave initially heated to 285 C and with a pressure, due to saturated steam, of 1000 psia. With transients of 84 and 180 Mw-sec (90 and 170 cal/gram of core material) on 139 and 140-msec periods, the pins reacted to the extent of 19.1 and 39.9 percent, respectively (based on clad and core).

Two transients on unclad plates of an 89.4 weight percent zirconium and 16.6 weight percent uranium alloy gave 6.0 and 67.2 percent zirconium-water reaction at energy inputs of 284 and 783 cal/gram, respectively. For this fuel, the input of nuclear energy, calculated by zirconium-95 fission analysis of natural uranium foil placed in each experimental assembly was determined to be 1.37 cal/(gm)(Mw-sec of reactor power).

V. Energy Conversion (pages 201 to 210)

Studies on regenerative emf cells are continuing with the object of converting nuclear energy into electricity.

An inert atmosphere of high purity is required for cell operations and basic studies of metal-salt behavior. A system of helium purification for a small glove box has been designed, assembled, and placed in operation. Gas purity achieved in the inert atmosphere boxes is very high, i.e., total contaminants are less than 30 ppm.

Phase studies by means of heating and cooling curves have been initiated in one of the inert atmosphere boxes. The apparatus is described.

Research on thermoelectric materials for direct conversion of heat into electricity has continued. Measurements are being made in the areas of liquid thermocouple systems and refractory solid thermocouple systems. During the present report period, Seebeck coefficients in the liquid indium-antimony system have been measured for 24 compositions in the range from 100 to 46 atom percent antimony for the mean temperature 750 C. At this temperature liquid antimony has a positive Seebeck coefficient which rises gradually as indium is added up to a composition of about 45 atom percent and then decreases as the indium content is increased to about 54 atom percent.

Seebeck coefficient measurements in the temperature range from 100 to 900 C have been made on a sintered uranium monosulfide ingot containing one percent by weight uranium oxysulfide. Seebeck coefficients ranged from ~ 70 mv/C at room temperature to ~ 90 mv/C at 800 C. Oxidation of the sample was found to result in a lowering of the Seebeck coefficient.

No Hall voltage was detected for a specimen of thorium monosulfide.

VI. Determination of Nuclear Constants (pages 211 to 217)

The number of capture, fission, and (n, 2n) reactions per 10^6 uranium-233 atoms is given as a function of the reactor horizontal and vertical positions in the EBR-I, Mark III loading. The number of capture and fission reactions per 10^6 uranium-235 and plutonium-239 atoms is given for the same loading and compared with previous results in EBR-I, Mark I loading.

The capture cross section of thorium-232 has been determined for monoenergetic neutrons in the energy range from 0.19 to 1.2 Mev. The shape of the curve agrees closely with the theoretical curve, showing a minimum in cross section with increasing energy near 0.4 Mev. Simpler nuclear theories would predict a continuous decrease in cross section with neutron energy in this energy range.

VII. Routine Operations (page 218)

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

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CHEMICAL ENGINEERING DIVISION SUMMARY REPORT

July, August, September, 1962

I. CHEMICAL-METALLURGICAL PROCESSING*

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

A. Pyrometallurgical Development

1. Melt Refining

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

The melt refining process will be used to recover uranium from the first core loading of EBR-II. The fuel is composed of approximately 50 percent enriched uranium alloyed with five weight percent noble metal fission product elements. The fuel pins, about $\frac{1}{8}$ in. in diameter, are clad with stainless steel and thermally bonded by a small amount of sodium. The pins are declad mechanically, chopped, and charged to a lime-stabilized zirconia crucible in which they are melted and maintained at 1400 C in a liquid state under argon for a period of 3 to 4 hr. Approximately two-thirds of the fission products are removed during this treatment through volatilization and selective oxidation. The purified metal product is top-poured to form an ingot from which new pins are prepared by injection casting. A mixture of oxides and unpoured metal remaining in the crucible as a skull is recovered by a separate process employing liquid metal solvents.

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

Experimental results for the quarter are reported on (1) an additional small-scale melt refining experiment with highly irradiated fuel, (2) methods of removing volatilized fission product iodine from the melt refining process off-gas, (3) the rapid nitridation of irradiated uranium-fissium fuel pins in nitrogen-argon atmospheres at high temperatures, and (4) yields of melt refining experiments with unirradiated fuel which had been stored for short periods in nitrogen-argon atmosphere.

a. High-activity-level Melt Refining Experiments
(V. G. Trice, W. H. Spicer)

A series of melt refining experiments utilizing highly irradiated uranium-fissium alloys has been conducted in order to reveal any hitherto undetected problems in the melt refining process which might arise from intense radiation and realistic fission product concentrations. A fifth and final experiment has been completed. A 382-g charge of EBR-II prototype fuel (10 percent enriched uranium-five percent fissium) irradiated to two total atom percent burnup and cooled for 25 days was melt refined under argon for one hour at 1400 C in a lime-stabilized zirconia crucible. The yield of purified metal was 73 percent. The fission product removal data are not yet available.

b. Behavior of Iodine and Other Volatile Activities
(V. G. Trice, W. Spicer, C. Honesty)

One of the purposes of the fifth high-activity-level melt refining experiment was to investigate the behavior of iodine during subsequent off-gas-handling operations. Knowledge of iodine behavior during these operations is required to establish specifications for the off-gas-handling facilities of the EBR-II Fuel Cycle Facility in order that the release of iodine-131 will not result in air concentrations in excess of the maximum permissible air concentrations established by the AEC. Currently, the AEC¹ has set the maximum permissible concentration of iodine-131 in air for 40 hr of human exposure in any period of seven consecutive days at 9×10^{-9} c/m³. Since discharged EBR-II fuel may contain at the time of processing as much as one curie of iodine-131 per gram of fuel (10,000 c per melt refining batch), a problem of iodine control is present.

Numerous safeguards have been included in the design of the Fuel Cycle Facility to minimize the possibility of the inadvertent release of activity. Included are containment of processing facilities in closed,

¹Federal Register, November 17, 1960; Title 10-Atomic Energy; Chapter 1, Atomic Energy Commission; Part 20, Standards for Protection Against Radiation.

inert-atmosphere cells, the use of large holdup tanks for off-gases in order to permit dilution and controlled release of gaseous activity to the atmosphere, and the employment of filter systems to remove particulate matter before discharge of gas from a 200-ft stack. These safeguards make the accidental release of radioactive iodine to the atmosphere highly improbable. In addition, studies of the behavior of iodine in the melt refining process, discussed later in this section, indicate that only a very small fraction of the iodine in the fuel is released as volatile activity. However, because of the ability of all materials of construction to remove by adsorption a portion of the iodine in a gas stream,²⁻⁴ a radiation hazard could develop in areas where lightly shielded off-gas-handling facilities are located. Therefore, it is desirable to remove iodine from melt refining off-gases as near the melt refining crucible as possible.

Experiments have previously been conducted with highly irradiated EBR-II prototype fuel (400-g melt refining experiments and 20-g fission product volatilization studies) at burnups of 0.22 to 2 atom percent and iodine-131 concentrations of up to one curie per gram. Important findings bearing on the behavior of iodine are as follows:

- 1) About 0.1 percent of the iodine in the charge material appeared in the ingot of purified metal after melt refining in one run (see ANL-6413, Table 1, page 35).
- 2) Melt refining of a 7-g charge of irradiated EBR-II fuel without pouring resulted in a 1.3 percent retention of iodine in the combined ingot and skull (see ANL-6569, Table 1, page 28).
- 3) Oxidation of the ingot and skull button from the above experiment resulted in a retention in the oxide of 0.25 percent of the iodine, relative to the concentration of iodine in the starting fuel material (see ANL-6569, Table 2, page 29).
- 4) Since most of the volatilized iodine in the experiment referred to in Item 3 was found condensed in a zone that had temperatures between 450 and 700 C, it appears that much of the iodine was not volatilized in the elemental form. It is strongly suspected that the iodine volatilized as

²Chamberlain, A. C., Eggleton, A. E. J., Megaw, W. J., and Morris, J. B., Behaviour of Iodine Vapour in Air, Discussions of Faraday Society, No. 30, 162-169 (1960).

³Silverman, L., Dennis, R., Kristal, E., and Stein, F., Iodine Collection Studies, TID-7593, 322-43 (1960).

⁴Bancroft, A. R., Watson, L. C., and Hewitt, R., Tests on Collectors to Remove Iodine from Ventilation Air, CRCE-981 (AECL-1131) (Oct 31, 1960).

cesium iodide, since cesium was present in the same temperature zone in excess of the stoichiometric requirement for cesium iodide. However, the total iodine accounted for in this experiment was only about 50 percent of that in the charge material (see ANL-6569, page 28).

5) From the high-activity-level melt refining experiments, it was determined that less than 0.005 percent of the iodine-131 activity originally in the charge (0.0018 c vs 40 c) appeared in the furnace argon atmosphere after melt refining and cooling of the furnace to equilibrium at ambient temperature (see ANL-6413, Table 3, page 39).

Off-gas-handling Facilities and Procedures for EBR-II Fuel Cycle Facility.

The Fuel Cycle Facility furnace will contain volatile radioactive fission products, principally xenon-133, krypton-85, and iodine-131, after melt refining. The furnace will be allowed to cool to equilibrium temperatures* and the gases will be removed before the furnace is opened. The gases will be pumped to a lightly shielded ($1\frac{1}{4}$ in. of steel) storage tank which is located just outside the Fuel Cycle Facility and where some decay of the short-lived xenon-133 and iodine-131 activities will occur. Gases from the tank will be disposed of through a 200-ft-high stack when meteorological conditions are favorable.

To minimize the shielding requirements of the subcell off-gas-handling apparatus (holdup tank, vacuum pump, filters, and piping), any iodine-131 in the off-gases must be largely removed before the gas reaches the subcell. In essence, an iodine trap is required that will efficiently remove iodine, in whatever form present, from argon and other off-gases and retain it at system pressures as low as a few millimeters absolute pressure. Iodine may be present in off-gases in at least two and possibly three forms:

- 1) elemental iodine present in molecular form in the gas stream;
- 2) particulate-carried iodine, either iodine-containing compounds or molecular iodine sorbed on dust; and
- 3) iodine as a constituent of some volatile compound (thought to be a remote possibility).

*The metal bell jar of the furnace will probably cool to between 40 C and 100 C, but if fully irradiated fuel is processed, the zirconia melt refining crucible will probably not cool to much below 650 C.

Experimental Equipment. For this investigation of the off-gas-handling operation following melt refining in the fifth high-activity-level experiment, the experimental melt refining furnace in the Chemical Engineering Hot Chemistry Cave was equipped with a radioactive-gas-storage system functionally similar to that planned for the Fuel Cycle Facility. This system, shown in Figure 1, provides for the removal of off-gases from the furnace and their delivery under pressure to a shielded storage cylinder. By using a gas pump, A, as the first stage and a compressor, B, as the second stage, it was possible to reduce the furnace pressure from atmospheric pressure to 10 mm in 75 min. Compressor B can maintain a 100-psig discharge at a suction pressure of 250 mm. The only modification required for the gas pump was replacement of the oil-level sight glass to permit operation at a discharge pressure as low as 250 mm.

Figure 1

EQUIPMENT FOR TRANSFERRING RADIOACTIVE GAS

The major differences between the plant-scale melt refining furnace and the smaller experimental melt refining furnace are:

- 1) use of a zirconia disc to cover the crucible in the experimental furnace instead of an inverted Fiberfrax* crucible which will be used over the plant melt refining crucible to trap condensable volatiles;

*A molded product of the Carborundum Corp. prepared from amorphous fibers using a colloidal silicon dioxide binder. The principal components of the fibers in weight percent are: alumina, 51.2; silica, 47.4.

- 2) an experimental furnace volume of 140 liters as compared with the plant furnace volume of 340 liters.

In previous experiments (see ANL-6569, pages 26 to 31), condensation of the major fraction of the recovered iodine (total recovery of about 50 percent) occurred on both Fiberfrax and nickel in a zone having temperatures between 450 and 700 C. This suggests that iodine deposition is mainly temperature dependent and not dependent upon the material on which it is being condensed. However, no data are available on the comparative rates of desorption from Fiberfrax and zirconia at reduced pressure.

The difference in furnace volumes may be of some significance with respect to the amount of molecular iodine adsorbed on surfaces, but it would have little effect on the objective of this study, namely, the determination of the ability of a particular charcoal filter assembly to remove iodine from off-gases during a furnace pumpdown.

A charcoal filter assembly for the removal of iodine, shown in Figure 2, was installed in the off-gas line between the experimental furnace and the gas pump. Included in this device were an AEC filter to remove particulate from the inlet gas, a seven-section bed (six $\frac{1}{2}$ -in. sections and one final $\frac{3}{4}$ -in. section) of activated charcoal, and a terminal

Figure 2
CHARCOAL FILTER ASSEMBLY FOR STUDY
OF IODINE REMOVAL FROM MELT REFIN-
ING FURNACE OFF-GASES

A. AEC Filter	1-5/8 in. Dia.
B. Porous SST Filter Support	1-1/4 in. Dia x 1/16 in. thick
C. Plexiglass Charcoal Holder	1.0 in. OD x 0.703 in. ID x 4 lg
D. Copper Tube Structural Support	1-1/3 in. OD x 1.047 in. ID x 6 in. long
E. O-ring (End Seals)	#513-28, 1-3/8 in. ID x 1/16 in. w
F. End Retaining Screen	3/4 in. Dia, 3/64 in. mesh
G. O-ring (Holder Seal)	#1820-15, 3/4 in. ID x 1/8 in. w

11 68 GRAMS OF PITTSBURGH COKE COMPANY TYPE PBL ACTIVATED CHARCOAL, 12 X 30 MESH

AEC filter to provide an indication whether or not any particulate-carried iodine remained in the gas stream after treatment. Copper was the principal material of construction used in the off-gas-handling system. At the iodine concentrations encountered in this experiment, adsorption of iodine on the copper pipe between the melt refining furnace and the iodine trap was not significant, as discussed in the footnote on page 37.

A gas-sampling port, shown in Figure 3, was installed in the effluent line from the iodine trap.

Figure 3
RADIOACTIVE-GAS-SAMPLING
APPARATUS

Samples were obtained by piercing a rubber diaphragm with a hypodermic needle and withdrawing gas into an evacuated bulb. Performance tests showed the rubber diaphragm to be capable of withstanding a pressure differential of one atmosphere without leakage after being punctured several times by a burr-free hypodermic needle.

Experimental Procedure. Immediately after casting of the melt refined metal in the fifth high-activity-level experiment, the crucible temperature was reduced to 650 C, and pumping of the radioactive gases through the iodine trap to the storage tank was begun. The crucible was maintained at an elevated temperature during pumping to approximate the maximum heating effects due to fission products anticipated under actual Fuel Cycle Facility operating conditions. After the furnace pressure had been lowered to 200 mm, however, the pump-down was terminated because of a failure

of the compressor diaphragm and a resultant release of radioactive gas in hazardous quantities. Samples of the gas leaving the iodine trap were obtained at 600 and 200 mm. The sample taken at 600 mm had a high level of xenon and krypton activity, its radiation level being about 250 mr at one inch.

After repair of the compressor, the crucible was cooled to equilibrium temperature (about 300 C) and the furnace gases were transferred directly to the radioactive-gas-storage tank (i.e., the charcoal trap

was bypassed) in order to remove the bulk of the xenon and krypton.* The furnace was then pressurized to 750 mm with argon, the crucible was heated to 650 C, and a final pumpdown through the charcoal filter assembly was conducted. In 110 min, the furnace pressure was reduced from 750 to 8.5 mm. Samples of off-gases leaving the iodine trap were obtained at furnace pressures of 600, 200, 50, 25, 12, and 8.5 mm.

Results. Gamma spectrometric analyses of the above samples by means of a 256-channel analyzer provided data appearing in Table 1, which show appreciable xenon-133 activity but no iodine-131

Table 1

ACTIVITY IN EFFLUENT GAS FROM IODINE TRAP DURING
FURNACE PUMPDOWN AFTER HIGH-ACTIVITY MELT
REFINING EXPERIMENT NO. 5

(An initial pumpdown was terminated at 200 mm because of equipment failure. The final pumpdown, for which data are given below, followed restoration of the argon pressure to atmospheric pressure, cooling to equilibrium temperature, transfer of the bulk of the xenon and krypton to storage by twice evacuating the furnace from atmospheric pressure to 8 mm, and after a third restoration of the argon pressure, heating to 650 C.)

Duration of Pumpdown (min)	Furnace ^a Pressure (mm)	Activity, $\mu\text{c}/\text{liter}^b$	
		Xenon-133 ^c	Iodine-131 ^d
0	750	-	-
1.8	600	840	Not detectable
12.7	200	72	Not detectable
37.1	50	35	Not detectable
54.3	25	69	Not detectable
90	12	18	Not detectable
110	8.5	14	Not detectable

^aFurnace volume: 140 liters

^bGas samples (100 cm³) were obtained at furnace pressure and a gas temperature of 25.6 C.

^cData are presented as μc of xenon-133 per liter of gas at 760 mm and 20 C.

^dThe detection limit for iodine-131 was 10^{-3} $\mu\text{c}/\text{liter}$ of gas at furnace pressure.

*In previous high-activity runs, a pumpdown of the unheated furnace resulted in the removal of less than 0.005 percent of the iodine present (see ANL-6569, page 37).

activity detectable above counter background activity. The gas samples obtained at the 600- and 8.5-mm pressures were contacted with alkaline solution (sodium hydroxide or sodium hypochlorite) to absorb any iodine activity present. A trace of beta activity slightly higher than counter background was detected in the absorbing solution from both gas samples.

About 250 μc of iodine-131 was removed from the furnace off-gases by the AEC filters and charcoal bed in the iodine trap (see Table 2). The gas samples showed that less than 1.0 μc of iodine-131 passed through the iodine trap; therefore, the total amount of iodine-131 removed from the furnace during the final pumpdown, neglecting any retention by the copper process lines,* was also 250 μc . Thus, of the

Table 2

IODINE DISTRIBUTION ON COMPONENT PARTS OF GRAPHITE FILTER
ASSEMBLY EMPLOYED IN PUMPDOWN OF FURNACE AFTER
HIGH-ACTIVITY MELT REFINING EXPERIMENT NO. 5^a

Component	Activity (μc) ^b	
	Iodine-131	Xenon-133
Inlet AEC Filter	182	c
Charcoal - First Section	68	1.5
Charcoal - Second through seventh sections	c	1.5 each section
Outlet AEC Filter	6.2×10^{-2}	c

^aA diagram of the graphite filter assembly is presented in Figure 2.

^bAppropriate decay corrections have been applied to provide parity.

^cActivity was below the detection limit of 10^{-4} μc .

*Molecular iodine is removed from gas streams by adsorption on all materials.⁵ Chemisorption of iodine by copper at room temperature has been suggested,⁶ and the percentage removal of iodine from gas stream by copper has been observed to be both concentration-dependent and erratic.⁷ The adsorption of iodine on copper falls off rapidly at concentrations below one mg of iodine per cubic meter. Particulate-carried iodine would not be adsorbed on process lines.⁵

No significant increase in the residual activity level of the copper process lines used for off-gas removal was observed during furnace pumpdowns of this and preceding experiments. The very low pick-up of activity by the copper off-gas lines indicates that the off-gases contained very little molecular iodine. Based on the total amount of iodine collected on the filter assembly, the total iodine concentration in the off-gases (active, inactive, molecular, and particulate carried) was of the order of 10^{-2} mg/m³ of gas at 760 mm and 26.5 C. At this iodine concentration level, copper at 26.5 C is not an efficient agent for the removal of iodine.⁷

⁵Chamberlain, A. C., Eggleton, A. E. J., Megaw, W. J., and Morris, J. B., Behaviour of Iodine Vapour in Air, Discussions of Faraday Society No. 30, 162-169 (1960).

⁶Silverman, L., Dennis, R., Kristal, E., and Stein, F., Iodine Collection Studies, TID-7593, 322-43 (1960).

⁷Bancroft, A. R., Watson, L. C., and Hewitt, R., Tests on Collectors to Remove Iodine from Ventilation Air, CRCE-981 (AECL-1131)(Oct. 31, 1960).

$1.7 \times 10^7 \mu\text{c}$ of iodine-131 activity available in the furnace, only 1.5×10^{-3} percent was removed by the pumpdown (again neglecting any deposition on the copper). Essentially all of this was retained by the graphite filter assembly, with not more than 6×10^{-6} percent ($1 \mu\text{c}$) appearing in the effluent.

Of the iodine collected on the components of the graphite filter assembly (see Table 2), 73 percent appeared on the inlet AEC filter, 27 percent in the charcoal bed, and 0.025 percent on the outlet AEC filter. Since AEC filters are not effective agents for removing elemental iodine from gas streams, it is believed that the iodine collected by the AEC filters was largely nonvolatile particulate matter. A 256-channel analyzer gamma scan of the inlet and outlet AEC filters showed similar activity patterns, namely, cesium, iodine, ruthenium, barium, zirconium, in decreasing order of magnitude figures (weight basis) of 10,000, 10, 1, 1, and 1, respectively. Since the ratio of inactive to active iodine is estimated to be 1000 to 1 (weight basis), cesium and iodine were collected by the AEC filters in roughly equal amounts. These data are consistent with previous findings, summarized at the beginning of this section, which suggest that after melt refining iodine is present in the furnace principally as cesium iodide.

All of the iodine retained by the charcoal bed was found in the first one-half inch. However, the presence of traces of activity on the

outlet AEC filter shows that some particulate-carried iodine was not removed by either the inlet AEC filter or the charcoal bed. Typically, AEC filters will remove from gas streams better than 99 percent of particles as small as 0.35μ over the face velocity range from 10 to 160 ft/min. Outside this range of flow rates, the filter has much less ability to retain submicron particles. As shown in Figure 4, AEC filter face velocities were within the most efficient operating range throughout the pumpdown. It may be concluded, therefore, that the furnace off-gases contained a very small amount of submicron, iodine-bearing, nonvolatile particulate capable of penetrating the iodine trap.

Figure 4

EFFLUENT GAS FLOW RATE DURING FINAL FURNACE PUMPDOWN AFTER MELT REFINING EXPERIMENT NO. 5

The amount of xenon-133 activity in the off-gas during the final pumpdown (see Table 1) indicates that purging does not effect the expected reduction of rare gas activity in the furnace. This is attributed to sorption and desorption of rare gases from internal surfaces of the apparatus. Prior to the pumpdown, the furnace atmosphere was purged by twice evacuating from 750- to 8-mm pressure and refilling with argon, as described in Table 1. Calculations indicate this would effect replacement of about 99.99 percent of the atmosphere originally present. If all the rare gas activity in the melt had been released to the furnace atmosphere, the amount to be removed by pumpdown after the purges would be 3×10^{-3} percent. The amount of xenon-133 removed from the furnace during the pumpdown was, however, substantially more than that calculated on the basis of the aforementioned assumption. Integration of the data presented in Table 1 over the pumpdown schedule yielded a value of 6.3×10^{-3} c of xenon-133 removed from the furnace during the pumpdown. This represents about 0.2 percent of the xenon-133 initially present. Thus, at least 20 times more rare gas activity was present in the furnace than would be predicted from the purge program. Apparently, some rare gas activity is retained in the furnace by sorption on surfaces or particulate matter and is later desorbed.

The data in Table 2 also show that about $10 \mu\text{c}$ of xenon-133 was retained on the charcoal bed in the iodine trap. Although this represents less than 0.2 percent of the rare gas activity removed from the furnace during the pumpdown, it may, because of the 10-yr half-life of the krypton-85 associated with the xenon, represent an important factor in problems associated with the handling and storage of discarded iodine traps.

The significant conclusions of the pumpdown study are summarized as follows:

- 1) After melt refining and several hours of cooling to permit the crucible temperature to reach equilibrium with the ambient temperature and to permit the possible adsorption on furnace surfaces of molecular iodine present in the furnace atmosphere, a pumpdown of the furnace to 8.5 mm will effect a release estimated to be of the order of 10^{-3} percent of the iodine present.
- 2) Essentially all iodine in the off-gases during a furnace pumpdown after melt refining can be removed by a trap consisting of an AEC filter, a bed of activated charcoal, and a terminal AEC filter.
- 3) The effluent from the iodine trap will contain of the order of 10^{-6} percent or less of the iodine originally present in the furnace.

4) Purging effects a lower reduction of the rare gas activity in the furnace than would be calculated assuming ideal displacement.

5) A small fraction, a few tenths of a percent, of the rare gas activity in the off-gases will be retained by a charcoal bed.

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

Some nitridation of declad irradiated fuel pins is expected to occur in the Argon Cell of the EBR-II Fuel Cycle Facility, since the argon atmosphere may contain as much as five percent nitrogen, and fission product decay heat will raise the temperature of the declad fuel. Because excessive nitride formation might have an adverse effect on the melt refining process by decreasing the yields and by allowing the nitrogen concentration to build up in the ingot, the nitridation rates of irradiated fuel pins have been investigated under conditions simulating those expected in the plant.

Fuel pins used for previous nitridation studies (see ANL-6231, page 47; ANL-6287, page 42) which had been thought to be unalloyed uranium were found in recent analyses to contain about five weight percent fission elements. The individual elements were present in the following amounts (w/o): molybdenum (2.5), ruthenium (1.9), rhodium (0.3), palladium (0.2), zirconium (0.1), and niobium (0.1). Therefore the nitridation rates reported earlier for unalloyed uranium apply to this uranium-fission alloy. The rates obtained with uncoated pins of this alloy agree closely with literature data for pure uranium,⁸ indicating that the presence of these fission metals has little or no effect on the nitridation rate. The rate data presented earlier for uranium-fission alloy (see ANL-6287, page 42), which contained 0.6 weight percent cerium in addition to the elements listed above, are also of interest. The cerium addition appears to increase the nitridation rate slightly.

A single nitridation experiment was performed recently, in which a uranium-five percent fission pin irradiated to 1.18 total atom percent burnup and cooled 100 days was exposed to 100 percent nitrogen at one atmosphere pressure and 650 C. As in previous nitridation rate experiments (see ANL-6287, page 42), the pin was suspended vertically in a quartz furnace tube by means of a platinum wire. The pin had been exposed to air at room temperature for about 30 min prior to the experiment. After the pin was exposed to nitrogen for about 20 min at 650 C, its nitridation rate accelerated rapidly, as shown in Figure 5.

⁸Adda, Y., Investigation of the Kinetics of the Reactions of Oxidation, Nitridation and Hydridation of Uranium, Gauthier-Villars, Editeur, Imprimerie Libraire, Paris (1958).

The temperature of the fuel pin itself was not measured during the experiment. In the course of the reaction, the pin expanded both longitudinally and radially. Examination of the pin on removal from the furnace revealed considerable distortion and evidence of severe nitridation.

Figure 5
NITRIDATION RATE OF IRRADIATED URANIUM
(10 PERCENT ENRICHED)-FIVE PERCENT
FISSIONIUM

Atmosphere:	Nitrogen
Temperature:	650 C
Burnup:	1.18 percent
Cooling Time:	100 days
Specific Activity:	4.26 c/g
Exposure to air prior to nitridation:	~30 min

As a result of these observations, four additional runs were made in order to investigate the ignition behavior of irradiated uranium-fissionium pins in nitrogen atmospheres. The experimental conditions are described in detail in Table 3. It will be noted that the total atom burnup was 1.1 percent, the cooling time 100 days, and the total activity varied between 25 and 32.6 c. To avoid depletion of nitrogen in the vicinity of the rapidly reacting pin, flowing argon-nitrogen atmospheres were used instead of the static system employed in all previous experiments. These atmospheres contained 100, 5.0, 1.0, and 0.5 percent nitrogen in argon at one atmosphere total pressure, and were passed through the sample chamber at a rate of 100 cc/min. The furnace and pin temperatures were monitored continuously during the experiments. The furnace temperature was raised about 10 C/min.

The results are summarized in Table 3. Because of experimental restrictions, it was necessary to conduct Experiments 3 and 4 with pins that had been exposed to air for one day, whereas the pins used in Experiments 1 and 2 were used the same day of removal from the storage capsule. The self-consistency of the results and the general appearance of the pins immediately prior to the experiments suggested that the data are probably valid, but they should not be regarded as conclusive. There appeared to be little or no difference in the nitridation rate behavior in 5 and 100 percent nitrogen; in both cases the reaction became self-sustaining at about 660 C. In 1.0 percent nitrogen the reaction was mitigated somewhat, and in 0.5 percent nitrogen there was no evidence of ignition.

It is suspected that ignition may be related to the rapid swelling of irradiated uranium-fissium alloys which occurs on heating at 600 to 700 C (see ANL-6287, page 38) and which results in a greatly increased area of exposed metal surface.

Table 3

SUMMARY OF IGNITION EXPERIMENTS WITH IRRADIATED
URANIUM-FISSIUM ALLOY IN NITROGEN-ARGON
ATMOSPHERES

<u>Fuel Pins (each experiment)</u>				
Number:	1			
Burnup, total atom percent:	1.18			
Cooling time, days:	100			
<u>Conditions</u>				
Gas flow rate, cc/min:	100			
Heating rate, C/min:	~10			
<u>Experiment</u>				
	1	2	3	4
Weight (g)	6.42	5.86	7.66	7.18
Total Activity (c)	27.4	25.0	32.6	30.6
<u>Activity of Volatile Isotopes (c)</u>				
Xe ¹³³	6.48 x 10 ⁻⁵	5.92 x 10 ⁻⁵	7.74 x 10 ⁻⁵	7.25 x 10 ⁻⁵
Kr ⁸⁵	2.78 x 10 ⁻²	2.54 x 10 ⁻²	3.32 x 10 ⁻²	3.11 x 10 ⁻²
I ¹³¹	2.57 x 10 ⁻³	2.34 x 10 ⁻³	3.06 x 10 ⁻³	2.87 x 10 ⁻³
<u>Atmosphere (percent)</u>				
Nitrogen	100	5.0	1.0	0.5
Argon	0	95.0	99.0	99.5
Prior Exposure to Air (days)	0	0	1	1
Temp at which Reaction Became Self-Sustaining (C)	660	660	730	-
Maximum Temp (C)	860	880	880	920
Temp of Fission Gas Release (C)	660	660	660	660
Time Period of Fission Gas Release (min)	6	16	21	30
<u>Appearance of Fuel Pin</u>				
Vertical Growth	yes	yes	yes	yes
Radial Expansion	yes	yes	yes	slight
Distortion	yes	yes	slight	no
Cracks	yes	yes	yes	yes

No further studies of nitridation rate are planned at the present time.

d. Effect of Nitridation of Unirradiated Fissium Pins on Melt Refining Yield
(G. A. Bennett, W. Pehl)

Melt refining yield, the pouring yield after holding uranium molten at 1300 to 1400 C for 3 hr in a calcium-stabilized, pressed zirconia crucible, has been found not to be appreciably affected (see ANL-6477, page 34) by the extent of pin nitridation occurring under storage conditions

which simulate those expected after irradiated EBR-II fuel pins have been decanned and chopped into 2-in. lengths and before they have been charged to a melt refining crucible. In melt refining experiments showing this, 2 kg of unirradiated pins were stored for a period of 2 hr, during which time the temperature of the pins was maintained at 350 C. This is the estimated temperature of a single layer of pin segments which have received two percent burnup and have been cooled for 15 days.

During the past three months, yield experiments were made in which the storage temperature was raised to 650 C. This temperature could be reached in a close-packed mass of pins after charging to a melt refining crucible. In the crucible, the pins will be exposed to an argon atmosphere containing up to 5 percent nitrogen while the bell jar cover is being positioned and sealed in place, after which the atmosphere will be replaced with pure argon.

Prior to experiments to determine melt refining yield, the rate of nitride formation was determined for bare uranium-five percent fission fuel pins. About 1000 g of pins were stored in a zirconia crucible at 650 C for 96 min in an argon atmosphere containing slightly less than six percent nitrogen. The nitridation rate at 650 C, calculated from the increase in pin weight of 0.8744 g, was about 43 times faster than the rate at 350 C, and was about 26 percent greater than that predicted from laboratory data obtained at 650 C. The present data are considered to be in good agreement with the laboratory data. The difference between the sets of data is attributed to the greater roughness of the surface of the pins used in this experiment, particularly at the sheared ends. In a similar experiment conducted at 350 C for 24 hr, the increase in weight was seven percent greater than that predicted by laboratory data.

The results of the new series of experiments for melt refining yield are given in Table 4. Run 345 was made to check the yields previously obtained (see ANL-6477, page 35) with uranium-fission pins stored at 350 C for 2 hr under a 5 percent nitrogen-argon atmosphere prior to melt refining. The yield of 94.6 percent agrees well with the average of 95.6 percent obtained in two runs of the earlier work. In Run 347, a blank run, uranium-fission pins were stored for 2 hr at 650 C under a high-purity argon atmosphere before being melt refined in the usual way. Run 346 was identical with Run 347 except that in Run 346 a 5 percent nitrogen-argon atmosphere was substituted for the high-purity argon atmosphere during the 2-hr storage period.

The yields in all runs lay in the narrow range from 94.6 to 95.6 percent. Previous experience on the 2-kg scale has shown this variation to be within experimental error. Consequently, it is concluded that storage of unirradiated fission pins under a 5 percent nitrogen-argon atmosphere for 2 hr at 650 C prior to melt refining has a negligible effect on yield.

Table 4

EFFECT ON MELT REFINING YIELD OF STORING UNIRRADIATED
EBR-II FUEL PINS AT 350 AND 650 C IN NITROGEN-CONTAINING
ARGON ATMOSPHERES

Storage Conditions

Time: 2 hr
 Temperature: As indicated
 Atmosphere: As indicated

Melt Refining Conditions

Temperature: 1400 C
 Time: 3 hr
 Atmosphere: Argon containing nitrogen at the indicated concentrations
 Crucible: Pressed, lime-stabilized zirconia

Run No.	Conditions of 2-hr Storage		Description of Charge		Melt Refining Yield (%)	N ₂ Conc. in Ingot (ppm)
	Temp (C)	% N ₂ Present ^a in Argon	Form	Weight (g)		
-	350	5.4 ^b	U-fissium pin + ~0.5 w/o Ce	1961 ± 3	95.6 ^c	
345	350	5.2 ^b	U-fissium pin + ~0.7 w/o Ce	1964	94.6	62 (exterior) 40 (interior)
347	650	0.02	U-fissium pins + ~0.7 w/o Ce	1964	95.5	<10 (composite)
346	650	5.0 ^b	U-fissium pins + ~0.7 w/o Ce	1964	94.7	191 (composite) 195 (interior)

^aAs the mass spectrometer cannot distinguish between nitrogen and carbon monoxide at these concentrations, a small amount of the latter may be present.

^bThe nitrogen concentration did not change significantly during the storage period.

^cAverage of two runs from previous series (see ANL-6477, page 35).

Significantly higher nitrogen concentrations were present in the product ingots of those runs (Runs 345 and 346) in which storage of uranium-fissium pins prior to melt refining was in 5 percent nitrogen-argon atmospheres as compared with that in the product ingot of a run (Run 347) in which nitrogen was essentially absent. However, the maximum nitrogen concentration present in a melt refined ingot was only 190 ppm, which should not present any problems in subsequent fuel operations.

It should be emphasized that in the above experiments the effect of a high radiation field was absent. Laboratory data have shown that at 500 C in 100 percent nitrogen the nitridation rate of an irradiated, sodium-coated pin was the same as that for an unirradiated sodium-coated pin (see ANL-6569, page 46); however, rapid nitridation of the irradiated pins occurred in 100 percent nitrogen at 650 C, at which temperature the pins also underwent considerable swelling.

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

Several processes are under development in which liquid metals and salts are employed as processing media. Work was continued on the development of the skull reclamation process for recovering the fissionable material remaining in the crucible residue (skull) after a melt refining operation. Development of this process has progressed to the stage of demonstration of process runs and the beginning of construction of large, integrated process equipment. A process has also been developed in which liquid metal solutions are used to achieve the isolation of plutonium bred into the EBR-II blanket material. Laboratory work is in progress on the development of processes for other fuel materials, especially future EBR-II cores, which will contain plutonium as a fissionable material.

Fundamental studies are also in progress in molten metal and molten salt systems. These include studies of reactions in molten salts and studies of various unit operations in liquid metal systems (e.g., distillation, mass transfer, and mixing).

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

The skull reclamation process is being developed as an auxiliary process to the melt refining process of the EBR-II fuel cycle. The process has two purposes: (1) recovery of the fissionable material from melt refining crucible residues, and (2) sufficient separation of this material from fission products to allow return of this material to the main EBR-II fuel cycle. Runs for demonstration of the skull reclamation process are being conducted on a 130-g-uranium scale in an inert-atmosphere glove-box described in ANL-6543, page 33. These runs, which are being made under argon according to the general flowsheet presented in Figure 6, are intended to test process variables and determine optimum process conditions prior to the operation of larger integrated equipment.

The uranium material balance and the fission product removals for the first demonstration run are presented in Tables 5 and 6. The uranium recovery is gratifying and apparently would have been of the

Figure 6

FLWSHEET FOR SKULL RECLAMATION PROCESS (Weights Relative to Initial Charge of Skull Oxide)

Table 5

DISTRIBUTION OF URANIUM IN SKULL RECLAMATION PROCESS. DEMONSTRATION RUN NO. BJ-4

Stream	Type of Stream	% of Charged Uranium ^a
Zinc Extract, containing Noble Metals	Waste	0.008
Flux from Skull Oxide Reduction	Waste	0.5
Supernatant Soln from Intermetallic Compound Precipitation	Waste	0.7
Supernatant Solution from Intermetallic Compound Decomposition	Waste	1.7
Samples and Recoverable Heels ^b	Product	10
Retorted Product Metal	Product	87

^aThe uranium present in the oxide charge was 141 g.

^bMost of the uranium in recoverable heels is present in the heel solution remaining in the oxide-reduction crucible. In repetitive operations, this uranium would not be lost.

Table 6

PRODUCT ANALYSIS FROM SKULL RECLAMATION
DEMONSTRATION RUN BJ-4

	<u>Skull Oxide Charge (g)</u>	<u>Uranium Product (g)</u>	<u>Percent of Charged Weight in the Product</u>
Uranium	141	123	87 ^a
Cerium	9.1	1.04	11
Zirconium	2.8	0.85	30
Ruthenium	1.9	1.57	83
Molybdenum	2.9	1.34	46
Magnesium	0	1.2	-

^aMost of the uranium not accounted for in this table remained in the heel left in the skull oxide-reduction crucible after transfer of the uranium solution.

The uranium in the heel would be recovered with the next batch of skull oxide processed.

order of 97 percent if the metal heel of the reduction step had been recycled. The recycle of this heel will be a normal process operation. A series of four additional runs were begun in which heels remaining after the noble metal extraction and uranium reduction were recycled. These runs were discontinued before completion to study difficulties in the noble metal extraction step discussed below. In all runs made to date, the equipment has worked well.

The fission product removals given in Table 6 for the first demonstration run indicate a satisfactory removal of cerium, poor removal of ruthenium, and a removal of molybdenum and zirconium which may be barely sufficient to meet process requirements. These fission product removals are discussed in detail below.

(1) Cerium Removal

As indicated above, the cerium removal was satisfactory. The extent of its removal in the process appears to be the same as the percentage of supernatant phase removed after decomposition of the intermetallic compound. More efficient phase separations than achieved here have been demonstrated in other laboratory-scale runs (see page 48, ANL-6569). Good phase separations should be more readily achievable in large-scale equipment than in the small-scale demonstration equipment.

(2) Zirconium Removal

Two sources of zirconium exist in the feed material of the skull reclamation process: zirconium introduced as a fission product, and zirconium introduced as zirconia crucible fragments in the operation of skull oxidation. The fission product zirconium introduced into the fuel will constitute about 0.25 percent of the fuel per reactor pass. The zirconium concentration in the skull material after melt refining and pouring has been slightly higher than in the fuel material (0.4 percent instead of 0.25 percent). If additional zirconium is introduced into the skull oxide as zirconia crucible fragments (to an expected maximum extent of one percent of the skull oxide) and if 70 percent of the zirconium is removed in Run BJ-4 (Table 6), the zirconium concentration in the product of the skull reclamation process for the first fuel cycle would be 0.48 percent (a net increase of 0.08 percent over that in the starting skull material). On subsequent cycles of fuel through the reactor and process, a net removal of zirconium would ultimately be achieved, but under the above assumptions, the equilibrium zirconium concentrations in recycled reactor fuel would be 5.4 percent entering the reactor and 5.7 percent leaving the reactor. An equilibrium zirconium level of only 1.6 percent would result if the process provided 100 percent removal of the zirconium. A zirconium concentration of up to $2\frac{1}{4}$ percent in EBR-II fuel has been shown to have no serious effects (see ANL-6116).

Because of the variability in zirconium input due to the nonreproducible amount of zirconia fragments included in each run, it is difficult to determine the zirconium removal required in the skull reclamation process, and the removal shown in Table 6 may be insufficient. Zirconium removal is an aspect of the demonstration runs which will be explored thoroughly. Its low concentration in product and feed materials has made chemical analysis difficult; therefore, future runs have been planned with zirconium tracer. However, because two sources of zirconium exist in skull oxide, the tracer results will require careful interpretation.

(3) Molybdenum and Ruthenium Removal

Poor removal of ruthenium and molybdenum is indicative of poor extraction of these elements in the noble metal-extraction step. These poor removals are in contrast with extraction of about 75 percent of the ruthenium (and greater than 75 percent extraction of molybdenum) achieved in previous demonstration experiments performed outside the glovebox (see ANL-6413, page 43). When this difficulty with the noble metal extraction was discovered, the performance of this step in the four subsequent demonstration runs was immediately determined and noble metal extraction found to be poor. These runs were, therefore, discontinued so that full attention could be given to the problem of noble metal extraction.

As indicated in Table 7, extraction of ruthenium appears to have been dependent on the flux-handling procedures. Runs in which the flux was exposed to air with associated opportunity to absorb water (the flux is highly deliquescent) provided good ruthenium extraction, whereas runs in which the flux was handled in fairly high-purity argon atmospheres resulted in virtually no extraction of the ruthenium. It is thought that the reaction of water with flux constituents, resulting in the formation of oxychlorides or hydrogen chloride and/or absorbed oxygen reacting to give chlorine, may have a pronounced beneficial effect on ruthenium removal in

Table 7

EFFECT OF FLUX COMPOSITION AND FLUX-HANDLING PROCEDURE
ON RUTHENIUM REMOVAL IN THE NOBLE METAL-EXTRACTION
STEP OF THE SKULL RECLAMATION PROCESS

Charge (average weights): 3 kg zinc, 750 g of flux composed (m/o) of CaCl_2 (47.5), MgCl_2 (47.5), and MgF_2 (5), and 130 to 190 g of skull oxide.

Conditions of Extraction: 4 hr at 800 C.

All runs were conducted in approximately $4\frac{1}{4}$ -in.-ID tungsten or tantalum crucibles. Agitation was considered good in all runs, although conditions were varied somewhat (stirrer speed was varied, and mixing baffles were sometimes present and sometimes absent). No significant effect of the agitation variations was detectable.

<u>Method of Flux Handling</u>	<u>Added Flux Constituents</u>	<u>No. of Runs</u>	<u>% Ruthenium Removal</u>
In argon atm ^a glovebox	None	5	10 ^b
In argon atm ^a glovebox	ZnCl_2 to 1 w/o concen- tion	1	63
In air for 5 to 15 min	None	6	75 to 90

^aThe argon atmosphere usually contained less than 100 ppm water and less than 20 ppm oxygen.

^bOne exception was a run made just following startup of the glovebox purification system. The salt flux was exposed for about 6 hr to an argon atmosphere estimated to contain 1000 ppm of water. A ruthenium extraction of 78 percent resulted.

the noble metal-extraction step. The addition of zinc chloride to the flux (see Table 7) also appeared effective in providing good extraction of ruthenium. Factors affecting the behavior of ruthenium in the noble metal-extraction step will be explored further.

The removal of molybdenum obtained in the first glovebox demonstration run (see Table 6) is considerably better than that for ruthenium. This is to be expected since, by virtue of its low solubility in zinc, molybdenum remains in the metal heel solution of the skull oxide-reduction step.

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

Isolation of the uranium metal product precipitated in the intermetallic compound decomposition step of the skull reclamation process (see Figure 6) requires a final retorting operation to remove the residual zinc and magnesium. Easy removal of the uranium product from the retorting crucible in high yield and in a form suitable for remote recycle to the melt refining process has been the primary objective of experimental investigations of the retorting operation.

The practicality of considering the uranium concentrate from the intermetallic compound-decomposition step (i.e., precipitated uranium enveloped in 50 weight percent magnesium-zinc alloy) as the end product of the skull reclamation process is also being investigated. The feasibility of this modification is dependent upon two conditions: (1) ability to remove this uranium concentrate from the decomposition crucible, and (2) ability to handle such a product in subsequent process steps. (In subsequent melt refining operation, for example, suitable provisions would have to be made for the collection of the zinc and magnesium vapors.)

Previous work has shown that only a ceramic crucible permits easy removal of the uranium in high yield, whether as isolated metal after retorting or as non-retorted uranium enveloped in residual zinc and magnesium. The ceramic material which has received the greatest attention to date is beryllia, which has the advantages over most other oxides of high thermal conductivity (and consequent low susceptibility to thermal shock) and high chemical stability. However, other less expensive ceramics, such as aluminum oxide and magnesium oxide, may prove to be suitable and will be evaluated in the future.

(1) Performance of a Metal-jacketed Isostatically Pressed Beryllia Crucible

Metal jacketing of a ceramic crucible may be desirable to minimize any deleterious results of metal leakage through cracks that may develop in the crucible. Testing of a stainless steel-jacketed, isostatically pressed, 4-in.-OD, $9\frac{7}{16}$ -in.-high beryllia crucible assembly (see ANL-6569, page 35) was continued during the past quarter. Three additional 120-g uranium scale runs (the fifth, sixth, and seventh tests made in this same crucible assembly) were conducted in accordance with the first two steps of the "three-step" procedure* described in ANL-6379, page 63. The uranium concentrate from the decomposition step (precipitated uranium enveloped in residual zinc and magnesium) was readily and completely removed from the beryllia primary crucible of the assembly in each of these latest runs. Isolation of the uranium metal present in these concentrates will be attempted in future experiments by retorting in an argon atmosphere at near-atmospheric pressure to evaporate the residual zinc and magnesium. It is planned to conduct these experiments in a modified, full-plant-size melt refining furnace.

Further testing of the jacketed crucible assembly used in the above runs has been terminated because the thin-walled rim of the crucible ($\frac{1}{8}$ to $\frac{1}{4}$ in. high) cracked away from the top of the primary crucible, resulting in a gap between the crucible and the stainless steel retaining ring, and permitting loss of beryllia powder which had been packed in the annulus between the beryllia and the stainless steel secondary. This problem will be avoided in fabricating future crucible assemblies by machining the stainless steel retaining ring instead of the beryllia crucible rim to achieve proper mating of parts. Except for this difficulty, the crucible was intact after the seven tests.

(2) Performance of a Metal-jacketed Thixotropically Cast Beryllia Crucible

As discussed in ANL-6477, pages 45 and 46, isostatically pressed beryllia crucibles have been prone to develop hairline cracks during initial use. These cracks have been attributed to internal stresses resulting from density variations inherent in pressed beryllia bodies. Consequently, thixotropic casting (casting in a mold a beryllia slurry which sets and may later be removed and fired) is being evaluated

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

as a suitable method for forming relatively stress-free beryllia crucibles. An additional advantage of this method of fabrication is its applicability to the economic production of large process-size crucibles.

Evaluation was initiated of a beryllia crucible assembly formed by jacketing a thixotropically cast beryllia crucible in stainless steel and tamping filling the annular space between the jacket and crucible with beryllia grain. During the past three months, the equivalent of ten 100-g-uranium scale runs were conducted in this assembly (of 4-in. OD by $9\frac{7}{16}$ -in. high) in general accordance with the "three-step" procedure referred to on p. 51. In all runs, the uranium concentrate (uranium enveloped in residual zinc and magnesium) was easily removable from the beryllia primary crucible after the intermetallic compound-decomposition step.

In one run the crucible assembly was subjected to a long-term test. To simulate conditions encountered in the precipitation steps, the uranium-zinc intermetallic compound was first precipitated, and then the melt was thermally cycled nine times between 800 and 450 C (i.e., alternate dissolution and precipitation of the uranium) before the bulk of the zinc-low magnesium solution was decanted. During this intermetallic-precipitation step, the melt was maintained above 450 C for 100 hr.

Magnesium (sufficient to form an ~50 percent magnesium-zinc solution) was then added at room temperature to the intermetallic residue remaining in the beryllia crucible. Decomposition of the intermetallic compound and subsequent precipitation of the uranium from the zinc-high magnesium solution was accomplished by heating the charge to 800 C. The melt was thermally cycled eight times between 800 and 450 C before the bulk of the supernatant zinc-high magnesium solution was decanted. During this intermetallic compound-decomposition step, the melt was maintained above 450 C for a total of 81 hr before being cooled to room temperature.

In the course of the long-term test, the metal-jacketed, thixotropically cast beryllia crucible was subjected to the equivalent of about eight intermetallic compound precipitations and eight decompositions, and was exposed to zinc-magnesium solutions at temperatures above 450 C for a total of 181 hr. Figure 7 provides a comparison of the conditions to which the metal-jacketed, thixotropically cast beryllia crucible was subjected in the long-term test with the conditions estimated for a plant-size crucible in the EBR-II skull reclamation process. The uranium concentrate resulting from the decomposition step of the long-term test was vacuum-retorted to remove the residual zinc and magnesium. Essentially 100 percent of the retorted uranium product was easily removed from the beryllia crucible. No visible deterioration of the internal surface of the beryllia crucible was evident after any of these tests. The presence of the

Figure 7

COMPARISON OF CRUCIBLE LONG-TERM TEST CONDITIONS WITH THOSE EXPECTED FOR EACH BATCH OF FUEL MATERIAL PROCESSED IN THE FULL-SCALE EBR-II SKULL RECLAMATION PROCESS

stainless steel jacket prevented inspection of the external surface of the beryllia crucible because the crucible could not be removed from the assembly without destroying the metal jacket.

Similar tests are to be conducted in this same crucible assembly in order to determine its useful life. Based on the above results, no serious problems are anticipated in the use of a metal-jacketed, ceramic crucible assembly in the intermetallic compound-precipitation and decomposition steps of the full-scale skull reclamation process.

(3) Performance of Unjacketed, Thixotropically Cast Beryllia Crucible

In order to inspect the external surface of a thixotropically cast beryllia crucible after use in the intermetallic compound-precipitation and decomposition steps, the equivalent of ten 150-g uranium scale runs were conducted in an unjacketed, thixotropically cast beryllia crucible (4-in. OD by 9 in. high). Two of these runs were performed separately. The remaining eight runs were portions of one test involving repetitive thermal cycles similar to that described above for the jacketed, beryllia crucible assembly. During this test, the unjacketed, thixotropically cast beryllia crucible was exposed to zinc-magnesium solutions at temperatures above 450 C for a total of 184 hr. The uranium concentrate (uranium enveloped in residual zinc and magnesium) was easily removed from the beryllia crucible in the two individual runs and the one long-term test.

Isolation of the uranium in the concentrate from the long-term test was accomplished by vacuum retorting to distill off the zinc and magnesium. The retorted uranium product was easily recovered in high yield from the unjacketed beryllia crucible. In future experiments, isolation of the uranium in the concentrate from the two individual runs by retorting at near-atmospheric pressure will be attempted.

No significant change was observed in the condition of the thixotropically cast beryllia crucible as a result of these tests. However, some deposits of metal beads were visible on the external surface of the crucible after the intermetallic compound-precipitation and decomposition steps of the tests. It has not been established whether this material diffused through the relatively porous walls (about 73 percent of theoretical density) of the thixotropically cast crucible or whether it condensed on the external surface of the crucible due to partial vaporization of the melt. In either case, the amount of material deposited was not considered large enough to cause any difficulties in full-scale process application.

(4) Discussion of Results

The results of the above tests in both metal-jacketed and unjacketed, thixotropically cast beryllia crucibles are the best obtained with any crucible material evaluated to date. These promising results, as well as the fact that this type of crucible can be fabricated in large sizes, indicate that thixotropically cast beryllia crucibles may be acceptable for the precipitation and retorting steps of the skull reclamation process. It is planned to procure larger thixotropically cast crucibles for performance evaluation.

c. Construction of Large-scale Integrated Equipment for the Skull Reclamation Process (J. C. Hesson, I. O. Winsch, K. Tobias)

Construction of integrated equipment for large-scale ($2\frac{1}{2}$ kg of skull oxide) demonstrations of the skull reclamation process is beginning. This equipment is believed to simulate closely the plant equipment. During the last quarter, a large glovebox in which the equipment is to be installed was received and set in position (minus windows and gloves). Installation of processing equipment in the glovebox has been started. Transfer lines and waste containers for the skull reclamation process were tested.

(1) Development and Testing of Transfer Lines (J. C. Hesson, G. Rogers)

At the present time, it is planned to effect liquid-phase transfers in the skull reclamation process by pressure-siphoning, a technique whereby solutions under pressure are transferred between vessels through top-entering pipes. It has been necessary to develop designs of transfer tubes suitable for fabrication from corrosion-resistant materials. The most suitable material of fabrication for transfer tubes and agitators found thus far is molybdenum-30 weight percent tungsten alloy (see ANL-6543, page 72, and page 70 of this report), which is sufficiently machinable to be fabricated into shapes. Although machinable, this alloy presents some problems since it cannot be welded, it is brittle, it oxidizes in air at high temperatures, and it is not available in normal tubing or pipe form.

A prototype, electrically heated transfer line was constructed according to the design shown in Figure 8 and was tested by being used to transfer zinc at various temperatures. This is the transfer line for the dual transfer-tube unit described on page 39 and illustrated in Figure 7 of ANL-6543. The molybdenum-tungsten alloy piping consisted of $\frac{1}{2}$ -in. rod with a $\frac{1}{4}$ -in. gun-drilled hole. The threaded elbows were

MOLYBDENUM-30 WEIGHT PERCENT TUNGSTEN
ALLOY TRANSFER LINE FOR THE SKULL
RECLAMATION PROCESS

The transfer line was used to make a series of 16 successful transfers of molten zinc involving about 8 kg of zinc per transfer. Two transfers were made at 550 C, five at 650 C, two at 700 C, one at 750 C, and six at 850 C. The highest transfer temperature encountered

in the skull reclamation process is 800 C. The transfer tube was subjected to increasingly severe conditions as it continued to show satisfactory performance. No difficulties were encountered in any of the transfers, and no deterioration of the transfer line was evident. It is planned to employ this transfer tube design in the integrated, large-scale ($2\frac{1}{2}$ kg of skull oxide) skull reclamation process equipment which is now under construction.

(2) Selection of Waste-container Materials for the Skull Reclamation Process
(J. C. Hesson, G. Rogers)

The principal waste materials from the skull reclamation process are: zinc removed in the noble metal-extraction step, a halide salt mixture which contains magnesium oxide and is removed after the reduction of skull oxides, an approximately four percent magnesium-zinc solution removed after the uranium-zinc intermetallic precipitation, and a 50 weight percent magnesium-zinc solution removed after decomposition of the intermetallic precipitate with magnesium. The most corrosive conditions encountered in handling these wastes are those associated with handling the zinc-rich solutions, which will be transferred to waste containers at about 500 C. With a view toward selecting simple waste containers fabricated of common but high-integrity materials, thin-wall (0.025-in.), type 18-8 stainless steel vessels were evaluated as waste receivers. After solidification of the waste metal or flux and being sealed, such vessels would have excellent resistance to exterior corrosion.

Five transfers of zinc into the waste receivers were made (see Table 8) by means of the transfer tube shown in Figure 8. The transfers were made at temperatures higher than the expected transfer temperature of 500 C in order to ascertain the margin of safety available with the thin-wall, stainless steel vessels. To simulate large batches and the heating provided by decaying fission products, both of which result in slow cooling rates, the containers were insulated with Fiberfrax* in four of the runs. Thermocouples were attached to the outside of the can. The time required for the zinc to cool to the freezing point and also the freezing time of the zinc were indicated by thermal arrests.

The containers were stripped from the zinc ingots for examination and, although the stainless steel was well "wet" by the zinc, there was no visible evidence of severe corrosion except at the transfer temperature of 850 C. Even at this temperature the receiver did not fail although it was severely attacked. On the basis of these results, the use of type 18-8 stainless steel containers for the collection of waste from the skull reclamation process appears to be feasible.

*Product of the Carborundum Company.

Table 8

TRANSFER OF MOLTEN ZINC INTO TYPE 18-8 STAINLESS
STEEL CONTAINER

Conditions:

Weight of zinc transferred: about 8 kg

ID of container: $5\frac{1}{8}$ in.

Thickness of container wall: 0.025 in.

Transfer Temp (C)	Insulation of Container	Time (min)		Final Condition of Steel Container
		To Cool to Freezing Point of Zinc	Freezing Time of Zinc	
550	None	10	30	Wet by Zn; no serious attack
550	Insulated ^a	20	58	Wet by Zn; no serious attack
650	Insulated ^a	26	53	Wet by Zn; no serious attack
750	Insulated ^a	35	48	Wet by Zn; no serious attack
850	Insulated ^a	45	45	Wet by Zn; formation of Zn-Fe intermetallic noted; no leaks; pene- tration of about $\frac{1}{2}$ of crucible thickness.

^aInsulation consisted of two layers of $\frac{1}{8}$ -in.-thick Fiberfrax, a product of the Carborundum Company.

d. Processes for Plutonium Reactor Fuels
(R. K. Steunenberg)

A promising fast reactor fuel is a plutonium alloy of approximately the following composition: uranium, 70 percent; plutonium, 20 percent; fission elements, 10 percent. One of the most difficult separations encountered in processing irradiated material of this type is that of obtaining adequate removal of rare earth fission products from the plutonium. Two promising methods for achieving this separation are being investigated. One involves selective extraction of the rare earths from a zinc-magnesium solution of uranium and plutonium by a molten halide flux. The other method

entails the use of a calcium-zinc solution in which the rare earths are soluble, and the plutonium and uranium are relatively insoluble. Further information has been obtained on the molten salt extraction technique during the past quarter.

Separation of Rare Earths from Uranium and Plutonium by Molten Salt Extraction

(J. B. Knighton, J. D. Schilb, J. W. Walsh)

The objective of this program is to investigate the possibility of separating the various elements present in spent reactor fuels by equilibration of the constituents of the fuel between molten zinc-magnesium alloys and a magnesium chloride flux. Distribution coefficients [$K_d = (w/o \text{ in flux}) / (w/o \text{ in metal})$] for yttrium, cerium, praseodymium, neodymium, uranium, plutonium, and americium between zinc-magnesium and magnesium chloride were summarized in ANL-6569, page 40. Additional distribution data have been obtained for thorium, vanadium, barium, and zirconium. In addition to the single-element distribution studies, the codistribution behavior of uranium, plutonium, and praseodymium has been examined. Data have also been obtained on the effects on distribution behavior of other variables, including the concentration of the element under study, the temperature of separation, the magnesium chloride concentration in the flux, and the substitution of cadmium for zinc in the liquid metal phase.

Single-element Studies

Thorium. Preliminary data for the distribution of thorium are shown in Figure 9. These data were obtained by approaching the equilibrium from the zinc-rich side of the magnesium-zinc alloy. Further experiments will be performed in which the equilibrium will be approached from the opposite direction. In general, thorium behaves much like uranium and plutonium, but it shows less tendency to return to the flux phase at high magnesium concentrations in the metal phase.

Figure 9
DISTRIBUTION OF THORIUM
BETWEEN ZINC-MAGNESIUM
ALLOY AND MAGNESIUM
CHLORIDE

Temperature: 800 C
Mixing Rate: ~300 rpm
Crucible: Tantalum
Atmosphere: Argon

Vanadium. Vanadium is of interest as a potential cladding material for reactor fuels. Preliminary results indicate that vanadium tends to favor the metal phase. However, nearly all the vanadium present disappeared from the system during the course of the experiments, suggesting either the volatilization of vanadium chloride or precipitation of the metal in the zinc-magnesium phase. Further studies of the behavior of vanadium are being made.

Barium. The distribution behavior of barium is presented in Table 9. No barium was detected in the metal phase. Although the material balance on barium was only 67 percent, none of the barium found was in the metal phase, thereby indicating that highly effective removal of fission product barium occurs on extraction with magnesium chloride. The low material balance probably resulted from the formation of solid barium oxide by reaction of barium chloride with residual magnesium oxide in the flux phase. Since filtered flux samples were taken, only the barium present in a soluble form appeared in these samples.

Table 9

DISTRIBUTION OF BARIUM BETWEEN ZINC-MAGNESIUM
ALLOY AND MAGNESIUM CHLORIDE

Conditions		Charge	
Temperature: 800 C		200 g zinc	
Mixing Rate: ~300 rpm		300 g MgCl ₂	
Atmosphere: argon		11.3 g barium	
Crucible: tantalum		467 g magnesium (added in increments)	
Sample No.	Metal Phase		Barium in Flux Phase (w/o)
	Mg (w/o)	Ba (w/o)	
1	0.766	< 0.01 ^a	2.43
2	13.77	< 0.01	3.04
3	47.2	< 0.01	2.52
4	76.2	< 0.01	2.38

^aBelow limit of detection.

Zirconium. Zirconium is of interest both as a fission product and as a possible constituent in cladding materials. The distribution data are given in Table 10. The results show zirconium favoring the metal phase at all magnesium concentrations between 0.08 and 75 weight percent. The behavior of zirconium at the low magnesium concentrations

was unexpected. It had been anticipated that at low magnesium concentrations zirconium would behave similarly to the other elements (rare earths, uranium, plutonium, and thorium) and distribute to the flux phase. In the first sample, the zirconium material balance was 98 percent. In subsequent samples containing more than about 10 weight percent magnesium in the metal, the decrease in zirconium concentration was greater than would be expected from the dilution effect alone. Possibly, zirconium precipitated in the liquid metal or losses resulted from the volatilization of zirconium chlorides. Although the results are subject to these possibilities and show considerable scatter, it is clear that zirconium shows a strong preference for the metal phase. Further studies of the behavior of zirconium are in progress.

Table 10

DISTRIBUTION OF ZIRCONIUM BETWEEN ZINC-MAGNESIUM
ALLOY AND MAGNESIUM CHLORIDE

Conditions		Charge			
Temperature: 800 C		200 g zinc			
Mixing Rate: ~300 rpm		300 g MgCl ₂			
Atmosphere: argon		10.3 g crystal bar zirconium			
Crucible: tantalum		467 g magnesium (added in increments)			
Sample No.	Metal Phase		Zirconium in Flux Phase (w/o x 10 ⁴)	Material Balance for Zr (%)	$K_d = \frac{\text{w/o Zr in Flux}}{\text{w/o Zr in Metal}} \times 10^4$
	Mg (w/o)	Zr (w/o)			
1	0.083	4.83	3.3	98	0.69
2	0.970	4.88	5.3	100	1.1
3	1.74	4.66	5.8	97	1.2
4	4.12	4.43	5.2	95	1.2
5	9.68	3.02	16	65	5.3
6	22.97	1.96	6.3	48	3.2
7	34.47	1.23	5.6	34	4.6
8	55.92	0.78	1.8	30	2.3
9	75.44	0.73	1.4	47	1.9

Codistribution of Uranium, Plutonium, and Praseodymium

An experiment was performed to determine whether the distribution coefficients for uranium, plutonium, and praseodymium in combination would differ from the values obtained with the individual elements in the zinc-magnesium alloy and magnesium chloride flux system. The conditions and results of the experiment are presented in Figure 10. The codistribution data, shown as solid points, agree with the

single-element results within the accuracy of the determinations. Thus, it appears from this experiment that separations of uranium, plutonium, and praseodymium can be based on the single-element distribution data.

Figure 10
CODISTRIBUTION OF URANIUM, PLUTONIUM, AND
PRASEODYMIUM BETWEEN ZINC-MAGNESIUM
ALLOY AND MAGNESIUM CHLORIDE

Temperature: 800 C
Atmosphere: Argon
Crucible: Tantalum

Effect of Concentration on the Distribution Coefficients of Uranium and Plutonium

Previously reported distribution data (see ANL-6569, page 42) indicated that the distribution coefficient for uranium between zinc-magnesium alloy and magnesium chloride is sensitive to the uranium concentration. This effect was confirmed by an experiment in which uranium was added progressively to a system consisting of zinc-10 weight percent magnesium in the metal phase and magnesium chloride in the flux phase. The results of this experiment, shown in Figure 11, reveal a marked decrease in the distribution coefficient at uranium concentrations below two weight percent. Also shown in Figure 11 for comparison are two points from previous experiments UE-1 and UE-2 (see ANL-6569, Figure 8, page 42).

The effect of the concentration of plutonium on its distribution coefficient was determined in a system identical with that used for uranium. The results are shown in Figure 12. These data show only a slight increase in the distribution coefficient as the plutonium concentration is increased. Agreement with previous data for plutonium (see ANL-6569, Figure 5, page 40) was less satisfactory than for uranium.

Figure 11

EFFECT OF URANIUM CONCENTRATION ON DISTRIBUTION COEFFICIENT

Temperature: 800 C
 Mixing Rate: 300 rpm
 Crucible: Tantalum
 Atmosphere: Argon
 Flux: 100 m/o MgCl_2
 Metal: Zn-10 w/o Mg

Figure 12

EFFECT OF PLUTONIUM CONCENTRATION ON DISTRIBUTION COEFFICIENT

Temperature: 800 C
 Mixing Rate: 300 rpm
 Crucible: Tantalum
 Atmosphere: Argon
 Flux: 100 m/o MgCl_2
 Metal: Zn-10 w/o Mg

Effect of Temperature on the Plutonium-Praseodymium Separation Factor

The effect of temperature on the separation of plutonium and praseodymium was investigated from 620 to 880 C. An equimolar lithium chloride-magnesium chloride flux was used instead of magnesium chloride alone, since the lower melting point of the mixture allowed a larger variation in temperature. The results are summarized in Figure 13 and Table 11. The logarithm of the separation factor [$\text{S.F.} = K_d(\text{Pr})/K_d(\text{Pu})$] increases linearly when plotted against the reciprocal of absolute temperature. This result suggests the possibility of using lower temperatures to increase the separation factor. Extrapolation of the data to 450 C indicates that a separation factor as high as 100 may be possible if a lower-melting flux system is used. This possibility is being investigated.

Figure 13

EFFECT OF TEMPERATURE ON PLUTONIUM-PRASEODYMIUM SEPARATION FACTOR

Mixing Rate: ~300 rpm
 Atmosphere: Argon
 Crucible: Tantalum

*Metal Phase: 48.5 w/o Mg (by analysis)

Table 11

EFFECT OF TEMPERATURE ON THE DISTRIBUTION COEFFICIENTS OF PLUTONIUM AND PRASEODYMIUM

Conditions		Charge
Mixing Rate:	~300 rpm	150 g zinc
Atmosphere:	argon	150 g magnesium ^a
Crucible:	tantalum	300 g 50 m/o LiCl-50 m/o MgCl ₂
		0.88 g praseodymium
		2.29 g plutonium

Temp (C)	$K_d = \frac{(w/o \text{ in flux})}{(w/o \text{ in metal})}$		S.F. = $\frac{K_d (Pr)}{K_d (Pu)}$
	Pu	Pr	
850	0.179	4.50	25.1
800	0.143	4.00	28.1
700	0.116	4.12	36.5
620	0.0885	4.13	46.7

^aChemical analysis indicated 48.5 w/o magnesium in the metal phase.

Figure 14

DISTRIBUTION OF PRASEODYMIUM AND
PLUTONIUM BETWEEN ZINC-50 WEIGHT
PERCENT MAGNESIUM AND LITHIUM
CHLORIDE-MAGNESIUM CHLORIDE FLUX

Temperature: 800 C
Mixing Rate: ~300 rpm
Crucible: Tantalum
Atmosphere: Argon

The results also show that the distribution coefficient of praseodymium remains nearly constant over the temperature range of the experiment. The variation in separation factor with temperature depends mainly on the change in the distribution coefficient of plutonium.

Effect of Magnesium Chloride
Concentration on the Codistribution
of Plutonium and Praseodymium

The effect of varying the magnesium chloride concentration in the flux on the codistribution of plutonium and praseodymium was determined for the system zinc-50 weight percent magnesium and a lithium chloride-magnesium chloride flux at 800 C. The results of this experiment, presented in Figure 14, show that the distribution coefficients of plutonium and praseodymium both vary with the magnesium chloride content of the flux. The separation factor, however, increases to about 33 as the magnesium chloride concentration is raised to about 30 mole percent, then remains constant at approximately that value throughout the rest of the composition range (see Figure 15). Extrapolation of the separation factor to 100 percent magnesium chloride (see Figure 15) gives a result that is consistent with the data obtained from distribution studies with the

Figure 15

EFFECT OF MAGNESIUM CHLORIDE CONCENTRATION IN FLUX ON PLUTONIUM-PRASEODYMIUM SEPARATION FACTOR

Temperature: 800 C
 Mixing Rate: 300 rpm
 Crucible: Tantalum
 Atmosphere: Argon
 Metal: Zinc-50 w/o Magnesium

individual elements. On the basis of these results, it appears that sufficient amounts of another chloride can be added to the magnesium chloride so as to reduce the melting point of the flux substantially without affecting the separation factor. This should permit operation at lower temperatures where the praseodymium-plutonium separation factor is larger, as previously discussed.

Effect of Substituting Cadmium for Zinc in the Metal Phase on the Codistribution of Plutonium and Praseodymium

The effect of substituting cadmium-magnesium for zinc-

magnesium as the liquid metal solvent was investigated at 650 C through the use of a 50 mole percent lithium chloride-50 mole percent magnesium chloride flux, selected because of its low melting point (~600 C). The results are presented in Figure 16, where the distribution coefficients of

Figure 16

DISTRIBUTION OF PRASEODYMIUM AND PLUTONIUM BETWEEN CADMIUM-MAGNESIUM ALLOY AND 50 MOLE PERCENT LITHIUM CHLORIDE-50 MOLE PERCENT MAGNESIUM CHLORIDE

Temperature: 650 C
 Mixing Rate: ~300 rpm
 Crucible: Tantalum
 Atmosphere: Argon

plutonium and praseodymium are shown as functions of the magnesium concentration in the cadmium solvent. The distribution coefficients for plutonium and praseodymium and the separation factors (shown in Figure 17) do not differ greatly on changing the solvent from zinc to cadmium at the same temperature. Although there appears to be no particular advantage in the use of cadmium for this separation, it represents an alternative system which could be employed if other process considerations made such a change desirable.

Figure 17

EFFECT OF MAGNESIUM CONCENTRATION IN CADMIUM ON SEPARATION FACTOR OF PLUTONIUM AND PRASEODYMIUM

Temperature: 650 C
Mixing Rate: ~300 rpm
Atmosphere: Argon
Crucible: Tantalum

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

When the plutonium concentration in the depleted uranium blanket material of the EBR-II reactor reaches about one percent, the blanket material will be processed to obtain the plutonium. Pyrometallurgical processes are under investigation for the separation of plutonium from uranium. In these processes the separation of plutonium from uranium is based on the high solubility of plutonium in magnesium-rich zinc alloys and the contrasting low solubility of uranium in these alloys.

(1) Blanket Process Demonstration Runs

The fifth of a series of blanket process demonstration runs,* summarized in Table 12, was completed in accordance with the usual procedure of dissolving the blanket material in a 12 to 15 weight percent magnesium-zinc alloy to produce an approximately 13 weight percent uranium solution, precipitating the uranium from solution by adding

*The results of previous blanket process demonstration runs are reported in ANL-6379, page 76; ANL-6413, page 56; ANL-6477, page 47; and ANL-6569, page 43.

The percentage removal of supernatant phase was 91.8, which compares favorably with values of 70, 87, 72, and 97 percent realized in four previous demonstration runs. It is believed that a 95 percent removal of plutonium-bearing supernatant would be readily achieved on a plant scale. A 95 percent phase separation (and therefore a corresponding 95 percent plutonium recovery in this step) may be sufficient because under reasonable reactor operating conditions, the value of the unrecovered plutonium is very small (about 0.05 mill/kwh).^{*} However, if higher plutonium recoveries are required, the uranium precipitate may be washed with additional 50 weight percent magnesium-zinc alloy. In this run, a plutonium-uranium separation factor^{**} of 230 was realized, as compared with a previous maximum value of 169. Essentially no entrainment of uranium occurred during transfer of the plutonium product solution. A separation factor of 230 is about the maximum that can be achieved at this point in the process. Use of a wash step to increase recovery of plutonium would be accompanied by a decrease in the plutonium-uranium separation factor and increased volume of the magnesium-zinc-plutonium supernatant solution. Additional separation of plutonium from uranium will occur during evaporation of the plutonium product solution, because uranium will precipitate from solution while zinc and magnesium are distilled.

Analytical results have not yet been obtained for another demonstration run which has been completed. Two additional demonstration runs will be made with lightly irradiated blanket material. Their purpose will be to determine the behaviors of iodine and other fission products in the blanket process.

(2) Separation of Magnesium-Zinc Supernatant Solutions

Two additional phase-separation runs were completed in a study of the separation of the magnesium-zinc supernatant from the precipitated uranium phase. These two runs, at a scale of approximately 5.5 kg of 50 weight percent magnesium-zinc and 500 g uranium, differed from the previous runs in the manner of magnesium addition during the precipitation step. In all previous runs, the melt from the dissolution step was allowed to cool to room temperature before sufficient magnesium was added to produce a 50 weight percent magnesium-zinc solution on later heating to 800 C. In these two runs, magnesium rods, $\frac{3}{8}$ in. in diameter and 36 in. long, were charged through the sample port into the dissolver solution (12 weight percent uranium-12 weight percent magnesium-zinc solution) which was at a temperature of 800 C. A solid uranium precipitate

^{*}This calculation is based on a two percent burn-up of fuel, a one percent buildup of plutonium in the blanket, and approximately equal rates of core and blanket processing.

^{**}Ratio of plutonium-to-uranium weights in product to those in feed.

was detectable when the magnesium concentration of the melt had reached about 40 weight percent. This method of magnesium addition was easily performed and would be readily adaptable to large-scale operations. In large-scale operations, use of this method would probably eliminate the need for additional melting vessels, transfer lines, and freeze valves.

After cooling to 400 C, phase separations of 96 and 94 percent were obtained in these runs. Calculations show that the uranium concentrations in the resulting uranium heel or concentrate were about 66 and 56 percent, respectively. No entrainment of the uranium precipitate occurred, as was indicated by the absence of a change in the uranium concentration in the supernatant phase before and after transfer. (The "after transfer" sample was taken from the transferred supernatant solution after that solution was heated to 800 C to dissolve any entrained uranium.) Table 13 shows the change in uranium concentration in the melt (from 0.9 weight percent to 0.37 weight percent) which resulted when the magnesium concentration was increased from 40.7 percent to 50 percent at about 800 C.

Table 13

URANIUM SOLUBILITIES IN MAGNESIUM-
ZINC SOLUTIONS

All samples were filtered through tantalum filters fitted in tantalum sample tubes.

Temp (C)	Melt Composition (w/o)		
	Zinc	Magnesium	Uranium
792	58.4	40.7	0.90
792	57.7	41.4	0.86
803	52.5	47.0	0.53
803	52.3	47.2	0.50
800	47.8	51.8	0.37
800	49.6	50.0	0.37

These two runs conclude the phase-separation studies on a 500-g-uranium scale. Results of runs which are now being made on about a 5-kg-uranium scale will be reported in the next quarterly report.

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

Studies are in progress to evaluate the compatibility of various materials of construction with liquid metal and salt systems of the types which may be employed in processes of fuel recovery. The

selection of materials for EBR-II processing equipment is the major objective, but data of more general interest are also being accumulated. Corrosion tests and performance tests under processing conditions are being used to evaluate materials. Methods of fabricating materials into items of process equipment are also being evaluated. Considerable attention was given during the past quarter to the fabrication of vessels from ceramic materials.

(1) Corrosion of Tungsten and Tungsten Alloys
(M. Kyle, M. Deerwester)

Previous experience (see ANL-6379, page 89; ANL-6243, page 14; and ANL-6543, page 64) has shown tungsten to be unattacked by zinc-magnesium solutions and fluxes containing magnesium chloride, lithium chloride, calcium chloride, magnesium fluoride, and zinc chloride at temperatures of 800 to 850 C. Most of this testing was done for periods of time near 100 hr in sealed tantalum corrosion capsules (for a description of the equipment and technique, see ANL-6287, page 74). However, tantalum does not possess sufficient corrosion resistance for containment of zinc-magnesium for long periods of time (see ANL-6379, page 89); therefore, long-term corrosion testing of tungsten must be done in other materials.

Long-term corrosion tests in zinc-flux media are complicated by the difficulty of sealing corrosion capsules fabricated of

materials (such as tungsten and molybdenum-30 percent tungsten) which are capable of withstanding the corrosive attack but which are brittle and not easily welded. Development of a mechanically sealed tungsten capsule is proceeding. In the interim, another method of exposing specimens to zinc-flux media has been employed. The materials to be tested were fabricated into agitator blades, four of which were fastened into a slot in a tungsten shaft by means of 0.040-in. tungsten wire, as shown in Figure 18. Use of several materials in one test is not ideal because of possible interactions. However, such interactions were considered unlikely, and, in addition, similar combinations of materials will be present in process operations. One 400-hr and one 500-hr run were made in

Figure 18
AGITATOR ASSEMBLY USED IN
CORROSION TESTING

which agitators of this type were rotated in the corrosion medium at 800 C. The zinc-flux corrosion medium was contained in a one-liter alumina crucible provided with four $\frac{1}{4}$ -in.-diameter tungsten rods for baffles. The materials evaluated, the test conditions employed, and the weight changes which resulted are shown in Table 14.

Table 14

CORROSION OF TUNGSTEN AND TUNGSTEN ALLOYS EXPOSED TO
THE SALT-METAL SYSTEM OF THE NOBLE METAL-EXTRACTION
STEP OF THE SKULL RECLAMATION PROCESS

(Samples were exposed as agitator blades on a tungsten shaft, as shown in Figure 18.)

<u>Sample Size</u>	0.090 in. by 0.225 in. by 1.5 in.		
<u>Conditions</u> (each run)	Time:	Run 1, 500 hr; Run 2, 400 hr	
	Temperature:	800 C	
	Metal Phase:	1350 g of zinc	
	Flux Phase:	425 g of composition	
		46.6 m/o LiCl	
		46.6 m/o MgCl ₂	
		4.8 m/o MgF ₂	
		2.0 m/o ZnCl ₂	
	Agitation:	460 rpm	
	Crucible:	Recrystallized alumina. Four baffles ($\frac{1}{4}$ -in.-diameter tungsten rods) were provided.	

Material	Initial Weight (g)	Weight Change ^a	
		(mg/sq cm) ^b	(percent)
Sintered Tungsten	8.5863	+2.2	+0.078 ^c
Rolled Tungsten Sheet	9.0848	-0.60	-0.020
70% Mo-30% W Alloy	5.4246	-69	-3.8
98% W-0.8% Fe-0.4% Ni Alloy	8.4880	disintegrated	

^aNo dimensional changes within the accuracy of measurement of $\frac{1}{2}$ mil occurred for the sintered tungsten, rolled tungsten sheet, and the molybdenum-30 percent tungsten alloy.

^bBased on flat side and end areas only.

^cDuring Run 1, the weight change for the sintered tungsten specimen was minus 0.22 percent. Weight changes for the other specimens were not obtained in Run 1.

Sintered tungsten and rolled tungsten sheet performed well, with only slight weight changes (see Table 14) and with no dimensional changes within the $\frac{1}{2}$ -mil accuracy of measurement. The molybdenum-30 percent tungsten alloy showed a weight loss of 3.8 percent, which is equivalent to approximately 5 percent of the molybdenum content. This weight loss is attributed to molybdenum leaching from the alloy, since molybdenum is soluble in zinc to the extent of about 250 ppm at 800 C. The sample did not undergo any detectable dimensional changes. In both runs, the tungsten-iron-nickel alloy was severely attacked. In the second run, the blade disintegrated, whereas the 0.040-in. tungsten wire used to hold the blade on the shaft was still intact. As a result of these tests, the tungsten-iron-nickel alloy has been eliminated from further consideration as a container material for zinc-flux systems. Tungsten shows adequate corrosion resistance for use as a container material for the zinc-flux systems used in these runs. Although the molybdenum-30 percent tungsten alloy does not have as good corrosion resistance as tungsten, it is believed to be adequate for certain purposes in which machinability is important (agitators and transfer piping).

The specimens which were tested are being cut by the electrical discharge method for bend tests and metallographic examination. In addition, the 70 percent molybdenum-30 percent tungsten specimen will be analyzed for molybdenum depletion.

Examination of some accessory parts used in the first run has been completed. No attack of the tungsten rods used as baffles was discernible by metallographic examination. The 0.040-in. tungsten wires used to hold the specimens in place were not detectably attacked. The heat shields, used in both runs, were fabricated of tantalum-10 percent tungsten alloy. The heat shields were badly embrittled, in some cases to the point of cracking. Metallographic examination showed severe intergranular attack.

The same agitator shaft assembly was used for both runs and thus was exposed for 900 hr to process conditions. The tungsten shaft showed no visible evidence of attack. The slot for the blades and the holes for the wire fasteners appeared to have retained their original dimensions, so that no corrosive attack or erosion was indicated.

A Type 304 stainless steel connector attached the tungsten shaft to a $\frac{3}{8}$ -in. stainless steel shaft which extended through the packing gland. The Type 304 stainless steel shaft was in satisfactory condition after the 900-hr exposure to the vapor phase (zinc and halide salt vapors).

Samples of each phase were taken from the solidified metal and salt after the first run and were analyzed for tungsten, molybdenum, nickel, and iron. The concentration of each element was below the detectability limits of spectrochemical analysis (100 ppm). Although leaching of molybdenum from the 70 percent molybdenum-30 percent tungsten alloy is suspected, molybdenum was not found in the zinc phase, possibly as a result of the taking of nonrepresentative samples caused by segregation during cooling of the ingot.

(2) Materials Demonstration Runs (G. A. Bennett, L. F. Dorsey)

Testing of materials for corrosion resistance is being performed with crucibles holding agitated liquid phases in order to duplicate

Figure 19

PRESSED-AND-SINTERED TUNGSTEN CRUCIBLE WITH INTEGRAL MIXING BAFFLES

(Crucible dimensions are: 5-1/4 in. OD, 12 in. high with wall thickness of 1/2 in.)

The molybdenum-30 percent tungsten alloy agitator is a 2 1/2-in.-diameter, three-bladed, marine-type propeller which is fastened by machine threads

processing conditions more closely than is possible in small-scale corrosion tests. Recently, a tungsten crucible made by isostatic pressing and sintering and a molybdenum-30 percent tungsten alloy agitator were tested in two separate experiments: (1) under skull oxide reduction conditions for 500 hr at 800 C and (2) under noble metal-extraction conditions, also for 500 hr at 800 C. These materials were chosen for the fabrication of equipment for these extended runs because their corrosion resistance and fabrication properties are the most promising for the stated applications.

The tungsten crucible, pictured in Figure 19, has smoothly rounded mixing baffles which were formed during pressing as an integral part of the crucible wall. The crucible cover and two heat shields which were suspended from it were made of 0.090-in. tungsten sheet.

to a $\frac{1}{2}$ -in.-diameter shaft of the same alloy. These parts were machined from swaged rod. The agitator shaft was attached to a stainless steel extension shaft at a point above the crucible cover.

In both parts of the run, the charge to the crucible duplicated the expected process conditions (except that noble elements were present in the skull oxide reduction portion). Specifically, for the oxide reduction portion of the run the charge consisted of the following: (1) metals (in weight percent): 91 zinc, 5 magnesium, 4 uranium added in the form of skull oxide; (2) salt flux (in mole percent): 47.5 magnesium chloride, 47.5 lithium chloride, 5 magnesium fluoride was added (in the amount of four times the weight of skull oxide). For the noble metal-extraction portion of the run, conditions were the same except that the metal phase was pure zinc instead of zinc-5 percent magnesium. Throughout the 1000-hr duration of the run, the agitator was operated continuously at 525 rpm.

At the conclusion of the 500-hr skull oxide-reduction portion of the run, the flux and metal were poured off together, and the

Figure 20

MARINE-TYPE PROPELLER FABRICATED FROM MOLYBDENUM-30 WEIGHT PERCENT TUNGSTEN ALLOY AFTER 1000-HR EXPOSURE TO SKULL RECLAMATION PROCESS MEDIA

Diameter of propeller is 2-1/2 in. Conditions: 500 hr under skull oxide-reduction conditions, and 500 hr under noble metal-extraction conditions (see Figure 6).

crucible and agitator were examined. The tungsten crucible had not undergone any visible attack. The agitator, made from molybdenum-30 percent tungsten, had undergone a pitting attack to a depth of about 20 mils. (The agitator as it appeared after 1000 hr of testing is shown in Figure 20.) The pits were more widely spaced on the shaft than on the blades of the agitator, indicating that the high-velocity flow past the blades increased the corrosion rate. Since this attack did not appear to be severe enough to discontinue use of the agitator, it was employed with the same tungsten crucible in the second part of the run under noble metal-extraction conditions for an additional 500 hr at 800 C. Again, the crucible appeared to be unaffected by the corrosion conditions: nor was additional corrosion attack apparent on the agitator. However, partway through the run, the agitator shaft broke in two as a result of abrasion by the tungsten crucible cover. Consequently, the agitator was immobile during part of the run.

In these runs the agitator and crucible were exposed to the corrosive conditions of the noble metal-extraction and reduction steps in the skull reclamation process for a period of time equivalent to 100 full-scale runs on each operation. From the good results obtained with the materials tested, it was concluded that a pressed-and-sintered tungsten crucible and an agitator made of molybdenum-30 percent tungsten alloy would adequately serve for noble metal-extraction and skull oxide-reduction conditions. With these results, and the success of molybdenum-30 percent tungsten transfer lines (see page 70) and thixotropically cast beryllia crucibles for the precipitation and retorting steps (see page 51), it is considered that adequate materials have been found for all of the critical applications, provided that no difficulties in fabrication or process performance are encountered with large-size vessels. Therefore, all future materials work will be directed toward completing the corrosion data, checking the performance of large-size vessels, improving the methods of fabrication, and finding less expensive materials.

(3) Containment of Molten Zinc-Magnesium-Flux Systems in Ceramic Vessels

(P. A. Nelson, Z. D. Jastrzebski,* G. A. Bennett)

Several ceramics, principally oxides, but possibly also carbides, are potentially useful container materials for the molten zinc-magnesium-uranium and halide salt systems encountered in the skull reclamation process. Beryllia, a material which has received considerable attention to date, is showing promise as a material in which to perform the precipitation and retorting steps of the skull reclamation process (see pages 51 and 54). However, further development of liquid metal and fused salt processes and their application in processing large quantities of nuclear materials may require the ability to construct large vessels. Of the metals, only tungsten and tungsten alloys have to date shown adequate corrosion resistance. However, at the present time, it appears that larger vessels can be fabricated from ceramics than from these metals. For this reason various ceramic oxides in addition to beryllia are being evaluated for their ability to contain typical process systems.

Containment of Salt Fluxes in Beryllia

(G. Bennett and L. F. Dorsey)

One drawback of ceramic oxide containers is the difficulty of containing molten salts in them because of the low viscosity and good wetting action of molten salts. Various attempts to contain molten halide salts in beryllia crucibles having densities of up to 90 percent of theoretical have failed as a result of excessive penetration of the crucibles by the salts.

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The possibility of sealing the mating surfaces of close-fitting beryllia pieces by the application of force on the uppermost layer was investigated. A crucible was fabricated of beryllia rings (2-in. ID by $1\frac{1}{2}$ in. high by $\frac{3}{8}$ in. thick) of high density (95 percent of theoretical) and having highly polished, close-fitting mating surfaces. The rings were pressed together by a weight resting on the top ring. However, the entire flux charge and a significant portion of the zinc charge leaked through the joints. This assembly would not contain water even when a large external pressure was applied, although mercury, which does not wet beryllia, could be easily contained. It was apparent from this result that joints in vessels fabricated from beryllia pieces will require some other method of sealing, and will probably need to be cemented.

Permeation of the ceramic itself by molten salts is also a problem. In the previous quarterly report (ANL-6569, page 51), it was reported that isostatically pressed beryllia with a density 92 percent of theoretical was completely permeated by a molten salt (47.5 m/o CaCl_2 , 47.5 m/o LiCl , and 5 m/o MgF_2) in 100 hr at 800 C. It was not surprising, therefore, to find even more permeation by a similar flux in a 24-hr test at 800 C of a beryllia crucible formed by casting a thixotropic slurry ($\frac{1}{2}$ -in. wall; density: 75 percent of theoretical). These observations indicate that a ceramic vessel which is fabricated by ramming or slurry casting, or consists of brickwork, will probably have to have its inner surface glazed or otherwise rendered impervious if it is to contain molten salts.

Fabrication of Ceramic Containers (Z. D. Jastrzebski, W. Pehl)

With the above problems in mind (permeation of molten salts through porous ceramic walls and leakage through joints), various materials and methods of fabricating large ceramic vessels were explored. Although beryllia crucibles appear to be satisfactory for the skull reclamation process, this long-range investigation is being undertaken in the hope that it will result in the development of techniques for fabricating crucibles from less expensive materials than beryllia.

For applications utilizing liquid metal solvents, the crucibles must withstand a maximum operating temperature of 800 C, with heat applied from the outside (unless direct induction heating of the melt is used). The materials also must be resistant to attack by magnesium-zinc-uranium-halide salt systems. Although the temperature requirement permits the use of low-melting ceramic eutectics, the presence of uranium prevents the use of common refractory carbides, such as silicon carbide, because of possible uranium carbide formation, and the presence of magnesium requires that stable oxides which will not be reduced by magnesium be used.

The initial approach has been to cast crucibles from a castable cement, similar to concrete. These crucibles will be fired to drive off the water of hydration. This approach involves the selection of a suitable aggregate, such as prefired beryllia, magnesia, or alumina, and the development of a hydraulic-type cement for a binder. The finished product will be fired at 1200 to 1500 C to obtain, it is hoped, a crucible which will have good thermal shock resistance and reasonably high thermal conductivity. In order to render the surface of this crucible impervious and capable of containing a flux, it will be necessary to provide a ceramic glaze on the interior surface.

Samples of castable cements (or "concretes") have been prepared for evaluation both by physical tests and by performance tests in which they will be exposed to process solutions. Two kinds of samples have been prepared: cylinders, of $\frac{3}{8}$ -in. diameter by $1\frac{1}{2}$ in. long for corrosion tests, and bricks, $1\frac{1}{2}$ in. x 3 in. by $\frac{1}{2}$ to 1 in., for physical tests.

Five cements prepared in the laboratory (compositions shown in Table 15) were used with fused alumina, magnesia, and beryllia aggregates in making the samples. Some of these cements might also be useful in making a mortar for beryllia bricks if brick construction is desirable. Cements 2, 3, and 4 began to harden in less than 15 min and are therefore more difficult to use than Cements 1 and 5, which hardened more slowly.

Table 15

COMPOSITIONS OF CEMENTS FOR BINDING
CASTABLE CERAMICS

<u>Cement</u>	<u>Composition (w/o)</u>				
	<u>CaO</u>	<u>Al₂O₃</u>	<u>MgO</u>	<u>SrO</u>	<u>BaO</u>
1	42	52	6		
2	7	39	5		49
3	10	40	5	45	
4	37.5	52.0			10.5
5	35	55		10	

An aggregate which had the proper size distribution to give a product of maximum bulk density was mixed with 8 to 10 percent cement by weight and with water (0.5 to 0.7 water-to-cement weight ratio) to produce a mixture of semiplastic consistency. The cement mixes were cast in steel molds, allowed to harden (hydraulic bond) for 16 to 24 hr, and fired, some at 800 C and some at 1200 C. The air-hardened samples had

apparent porosities of 3 to 8 percent, whereas the fired samples, from which the water of hydration was removed by firing, had porosities of 15 to 25 percent. The firing temperature did not greatly affect the porosity. However, those samples fired at 1200 C were stronger than those fired at 800 C, indicating the formation of some ceramic bonding at 1200 C.

Experimentation with materials for providing an impervious coating to the interior of the crucible is beginning. Silica, the major constituent in most commercial glazes, will not be used in this application because it would be reduced by magnesium.

g. Supporting Chemical Investigations
(R. K. Steunenber)

Both liquid metals and molten salts are used extensively in the pyrometallurgical processes proposed for EBR-II fuels. Fundamental chemical information on these systems is needed to guide the process development work and to provide an understanding of variables in process flowsheets. Work during the quarter has been devoted mainly to a final determination of the lithium chloride-magnesium chloride phase diagram.

(1) Phase Diagram of the System Lithium Chloride-Magnesium Chloride
(A. F. Messing, M. D. Adams)

Molten salt fluxes composed primarily of lithium chloride and magnesium chloride are being considered for use in the reduction of uranium oxides by zinc-magnesium alloys. A

Figure 21

LITHIUM CHLORIDE-MAGNESIUM
CHLORIDE PHASE DIAGRAM

preliminary determination of the phase diagram of this system was reported in ANL-6477, page 68. Additional thermal analysis data, supplemented by optical microscopy and X-ray diffraction information obtained at room temperature, have resulted in the final version of the phase diagram shown in Figure 21. Also shown in Figure 21 for comparison is the diagram reported by Sandonnini.⁹

Anhydrous lithium chloride was prepared by the

⁹Sandonnini, C., Gazz chim. ital., 44, 377 (1914).

method of Hill and Osteryoung.¹⁰ Anhydrous magnesium chloride was purified by vacuum sublimation. The required amounts of the two salts were sealed in tantalum capsules by electron beam welding under an inert atmosphere. Prior to the determinations of differential thermal analysis, the salt mixtures were fused at 800 C. The liquidus curve was determined by cooling the samples at the rate of 1 to 5 C/min. To determine the solidus, the sample was remelted, quenched, and equilibrated about 20 degrees below the expected solidus temperature for 24 hr. The temperature was then increased at the rate of one Centigrade degree per minute to determine the solidus point.

The data indicate the existence of a continuous series of solid solutions across the entire composition range, rather than of the two solid solutions inferred previously (see ANL-6477, page 68). The major difference between this diagram and the single literature reference⁹ (see Figure 21) is that the Argonne work shows generally higher liquidus and solidus temperatures and a relocation of the minimum from 40 to 33 mole percent magnesium chloride.

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

Engineering studies of liquid metal systems are in progress in the areas of liquid metal boiling, mass transfer, and mixing. Related to the mass transfer studies are measurements of the diffusivity of uranium in liquid bismuth.

(1) Metal Distillation and Boiling Studies

Performance of Large-scale Cadmium-distillation Unit

(J. F. Lenc, P. A. Nelson, R. Paul, J. Arntzen)

In the preceding quarterly report (ANL-6569, page 58), it was indicated that at high evaporation rates entrainment of liquid cadmium in the vapor was suspected. Several runs were conducted in the past quarter with tin as a nonvolatile solute in the cadmium to indicate the extent of any entrainment. However, sufficient runs have not yet been made to justify firm statements on the extent and pattern of entrainment.

In the course of these runs, previously achieved rates of evaporation of cadmium in excess of 65 kg/hr could no longer be attained because power inputs that would give high evaporation rates resulted in

¹⁰Hill, D. A., and Osteryoung, R. A., Chemical Behavior of Uranium and Thorium in Fused Salts, BNL-588 (Sept 30, 1959).

excessive (near 800 C) temperatures of the copper induction coil. A maximum evaporation rate of only 43 kg/hr could be attained.

During previous runs, the induction coil had retained an oxidized surface which was maintained (not deliberately) by a slow leakage of air into that portion of the equipment that houses the induction coil. The air leakage, which had persisted despite many attempts to eliminate it, was finally corrected through a change in the equipment design. In the resulting low-oxygen argon atmosphere, the copper oxide coating decomposed, leaving the coil surface bright and shiny, and decreasing the emissivity of the coil. In the temperature range from 700 to 800 C, emissivity values (relative to a perfect black-body condition) are from 40 to 80 percent for oxidized copper and only from 3 to 15 percent for cleaned or polished copper.¹¹ Since the induction coil is cooled primarily by radiation, an unoxidized coil would operate at a higher temperature at a given power input than would an oxidized coil.

In order to increase the emissivity of the coil for use in the oxygen-deficient system, the coil was plasma-arc flamed-sprayed

Figure 22
DEPENDENCE OF OPERATING TEMPERATURE OF COPPER INDUCTION COIL ON SURFACE CONDITION IN LARGE-SCALE CADMIUM-DISTILLATION UNIT

(Cadmium was distilled in all runs at a temperature of about 560 C.)

with aluminum oxide powder.* (At 800 C, the emissivity of aluminum oxide is 45 to 60 percent that of a perfect black body.) The effect of the three surface conditions of the coil on its operating temperature is shown in Figure 22. It is clear that high-emissivity surfaces make possible operation at high power inputs without generation of excessive coil temperatures. With the coated coil, evaporation rates of 69.5 and 86.5 kg/hr were achieved in two runs which had power inputs of 30 and 35 kw and maximum coil temperatures of only 690 and 725 C.

Study of Mechanisms of Liquid Metal Boiling and Entrainment (J. Wolkoff, J. T. Hepperly)

The nature and magnitude of the boiling and entrainment phenomena of liquid metals may differ greatly from those of water because of large differences in physical properties of the two types

¹¹Goldsmith, A., Waterman, T. E., and Hirschhorn, H. J., Handbook of Thermophysical Properties of Solid Materials, Vol. I, p. 253, The Macmillan Co., New York, N.Y. (1961).

*Flame spraying performed by R. Friddle of Argonne National Laboratory, Institute of Nuclear Science and Engineering.

of liquids (e.g., their thermal conductivity and surface tension). Although aqueous systems have been studied extensively, liquid metal systems have received little or no fundamental study.

The mechanism by which vaporization occurs during boiling affects the formation and entrainment of droplets by a vapor stream. At low pressures and low to moderate heat inputs, vaporization is likely to occur from the surface with no bubble formation (here called nonturbulent vaporization). At high heat inputs and high pressures, turbulent boiling (bubble formation beneath the liquid surface, which includes nucleate boiling at the heat transfer surface) is likely to occur. There is no sharp line of demarcation between the two regimes, and the liquid head (a combination of liquid density and height of liquid in the boiler) should also affect the location of these regimes.

An initial study of vaporization without bubble formation (nonturbulent vaporization) is being made with pure mercury in glass equipment. The metal is vaporized, condensed, and then returned by gravity in a closed system. Two mercury pool geometries have been utilized: a shallow pool (of $2\frac{5}{8}$ -in. diameter by $1\frac{7}{8}$ in. high) and a deep tubular pool (of 1-in. diameter by $8\frac{1}{2}$ in. high). The deep pool boiling loop is shown in Figure 23.

At low pressures (1 to 10 mm of mercury), nonturbulent vaporization at rates as high as 55,000 Btu/(hr)(sq ft) [2.1 lb-moles of mercury/(hr)(sq ft)] at the top surface of the shallow pool was previously reported (see ANL-6569, page 59). Preliminary measurements indicate that in the deep pool vaporization rates about double the above value can be achieved without

bumping at similar low pressures. Irregular bumping begins at higher heating rates, i.e., above about 110,000 Btu/(hr)(sq ft).

High-speed motion pictures were taken of the vaporizing surface of the deep pool boiler during nonturbulent vaporization. As the heat input and vaporization rate increased, a rapid and cyclic surface movement began and continued until the heat input was large enough to

cause bumping. The surface patterns, although changing with heat input, were not affected by the method of heating (resistance or 10-kc induction heating). This suggests that natural convection flow patterns near the vaporizing surface also were not affected by the method of heating.

The temperature within the vaporizing mercury in the deep pool boiler was found to fluctuate randomly. In one case the variations had a range of 40 C at an average liquid temperature of 175 C. In order to follow these rapid changes and to study later the changes that occur during bumping, a fast-response liquid metal thermocouple was used. The signal from the thermocouple is read on a cathode ray oscilloscope after amplification. Further development of this thermocouple is under-way to improve its capabilities, e.g., use of smaller hot junctions in order to approach point temperatures, and elimination of extraneous "noise" in the amplified signal.

Figure 23 shows the glass boiling loop and the stainless steel probes which formed the liquid metal thermocouple with the mercury. The signal appearing on the oscilloscope represents the voltage (amplified) caused by the difference in mercury temperature in the boiler and the condensate. Since the condensate was at an essentially constant temperature, the voltage changes represented temperature fluctuations of the mercury in the boiler. Figure 24 is a photograph of typical oscilloscope fluctuations during nonturbulent vaporization at low pressure (1 to 10 mm of mercury). The vertical temperature scale shown is an approximation

Figure 24

OSCILLOSCOPE TRACE OF TEMPERATURE FLUCTUATIONS DURING
NONTURBULENT VAPORIZATION OF MERCURY

(Average temperature: 179 C; pressure 1 to 10 mm of mercury)

based on an assumed linear emf-temperature relationship for the stainless steel-mercury thermocouple between room temperature (the operating temperature) and the normal boiling point of mercury. The average temperature of the vaporizing mercury near the surface was 179 C. The hot-junction probe was on the centerline and slightly submerged in the mercury. The temperature fluctuations represented on the trace have a range of nearly 30 degrees Centigrade.

During nonturbulent vaporization, the temperature fluctuations are small at low heating rates and increase as the heating rate increases. The maximum fluctuation observed with this method was about 48 C. During bumping the pattern changes recognizably.

Normal nucleate boiling at atmospheric pressure was also studied. A differently shaped trace was obtained. Figure 25 is a trace typical of nucleate boiling taken, in this case, at atmospheric pressure; the vertical temperature scale is the same as in Figure 24. The rapid and large temperature fluctuations have disappeared.

Figure 25

OSCILLOSCOPE TRACE OF TEMPERATURE FLUCTUATIONS DURING
NORMAL NUCLEATE BOILING OF MERCURY

(Average temperature: 357 C; pressure: 1 atmosphere)

Further work with this and similar liquid-metal thermocouple systems is planned. The origin of the fluctuations and the nature of the temperature distribution within the liquid immediately before and after bumping will be studied.

(2) Power Requirements for Mixing Liquid Metals
(R. D. Pierce, D. R. Armstrong*)

Measurement of power requirements for mixing liquid metals was undertaken to obtain mixing power correlations for liquid metals (e.g., Power number** as a function of Reynolds number**). Immediate practical reasons exist for obtaining mixing power data in liquid metals: (1) the necessity of specifying power requirements for mixing in liquid metal processes, particularly for scale-up of these processes, and (2) the necessity of having accurate mixing power information for use in mass transfer studies in agitated liquid metal systems.

The development of techniques and equipment has occupied considerable attention. Measurements of mixing power input into mercury were first made calorimetrically. This method was abandoned because of the tediousness of individual measurements, because accurate measurements of power input could be obtained only at relatively high power inputs, and because of anticipated difficulties in making measurements at high temperatures.

Subsequently, two other methods of power measurements, which had been used by the majority of investigators, were tried: (1) measurement, by means of a torque table, of the torque transmitted to the vessel, and (2) measurement of the torque transmitted by measuring the twist of a torsion shaft. Neither of these two methods had the simplicity of operation nor sensitivity throughout the range of power input that was desired.

The method which was ultimately developed and adopted was based on the reaction torque on the motor housing. The equipment (see Figure 26A and 26B) is simple and provides considerable sensitivity in power measurements. The motor housing is suspended vertically by a short length of music wire. A single low-friction bearing at the junction of the wire and motor housing serves to position the motor and give it radial support. The motor shaft is coupled to a $\frac{1}{2}$ -in. shaft by means of a short length of heavy music wire. The $\frac{1}{2}$ -in. shaft is positioned by two radial support bearings and is ultimately coupled to the agitator being tested. Provisions have been made to house the agitation vessel in a bomb

*Temporary summer employee.

**Power numbers and Reynolds numbers are dimensionless groups frequently used in correlation of mixing power data. The power number is $Pg_c/D^5\rho N^3$ where P = power, g_c = gravitational constant, D = characteristic dimension, ρ = density, and N = stirrer speed, all in consistent units. The Reynolds number is $D^2N\rho/\mu$, where μ is viscosity and the other symbols have the same meaning as in the Power number.

Figure 26
MIXING DYNAMOMETER

a. Drawing of Mixing Dynamometer

b. Photograph of Mixing Dynamometer

in order to permit operation under an inert atmosphere and with metals having toxic vapors. The radial support-bearing assembly is mounted on the flange cover of the bomb. The flange cover is equipped with a gas seal.

To make a measurement of reaction torque, the agitator rotational speed was first adjusted to the desired value and maintained at this value. Weights were then added to the balance pan until sufficient torque (product of weight and lever arm) had been provided to restore the motor to the position of zero speed. The torque measured in this way is equal and opposite to that caused by rotation of the agitator in the test fluid. The power input to the fluid is the product of the torque and agitator rotational speed. The sensitivity of the torque measurements with this apparatus is $\pm \frac{1}{2}$ in.-g for shaft speeds from 0 to 2500 rpm. The rotational speed was measured by a photocell which responded to alternate silvered and dull black halves of a portion of the shaft assembly.

Experimental Results. Runs have been made in both mercury and water systems. All of the mercury runs and some water runs have been made in a $4\frac{7}{8}$ -in.-diameter cylindrical flat-bottom tank. The other water runs, which were performed for comparison with published data, were made in 12-in.- and 13-in.-diameter vessels of the same shape. Mixing baffles, when present, consisted of four, vertical, equal-spaced baffles running the full height of the vessel and having widths equal to about ten percent of the tank diameter.

Most of the data have been obtained with flat two-bladed paddles, ranging in length from 1.3 in. to 6 in. Several runs were made with six-bladed turbines (blades attached to a flat disc) having 2-in., 4-in., and 6-in. outside diameters and with diameter-to-blade length-to-blade width ratios of 20:5:4.

The validity of data obtained by measurements of reaction torque was determined by making measurements in water with turbine systems and paddle systems which duplicated those used by other investigators. The turbine data agree well with turbine data of Rushton, Costich, and Everett¹² when the latter data are corrected by a factor of 0.87 as recommended by later investigators (see Figure 27).^{13,14} However, the paddle data are in poor agreement with the data obtained by Rushton and coworkers.¹²

In Figure 28 are presented power measurements in water and mercury using paddles of two sizes. It may be seen that for the $1\frac{5}{8}$ -in. by $\frac{17}{32}$ -in. paddle the mercury and water data fall on the same

¹²Rushton, J. H., Costich, E. W., and Everett, H. J., Chem. Eng. Prog., 46, 395 (1950).

¹³Oldshue, J. Y., and Gretton, A. T., Chem. Eng. Prog., 50, 615 (1954).

¹⁴Oldshue, J. Y., Personal communication to S. A. Miller.

horizontal line. Since in this region of Reynolds numbers the Power number should be a constant, this is indicative that correlations for aqueous systems are applicable to metals. Calorimetric measurements and reaction-torque measurements for a 3-in. by 1-in. paddle operating in mercury are also shown and are in good agreement. The accumulation of additional data on the effects of geometric variations should allow a general correlation to be developed which incorporates the effects of geometric variations.

Figure 28

MIXING POWER CORRELATIONS IN WATER AND MERCURY

Tank Diameter: 4-7/8 in.
Four baffles, each 10 percent of tank diameter.
Paddles positioned 1/4 in. off bottom.

Figure 27
COMPARISON WITH LITERATURE VALUES OF MIXING
POWER DETERMINATIONS IN WATER BY MEASURE-
MENTS OF REACTION TORQUE ON MOTOR

Tank Diameter: 13 in.; 4 baffles, each 8.6% of tank diameter.
Agitators positioned 4 in. above tank bottom.
Turbine Diameter: 4 in.; 6 blades, each 1 in. long by
0.80 in. wide.
Paddle: Blade, 4 in. long by 2 in. wide.

(3) Determination of Uranium Diffusivity in Liquid Bismuth (H. Hootman, J. C. Hesson)

Diffusivity measurements of uranium in liquid metal solutions were extended to measurements of the diffusivity of uranium in liquid bismuth. The diffusivities of uranium in cadmium and in zinc have previously been reported in ANL-6477, page 69, and in ANL-6569, page 60, respectively. As is reported here, the diffusivity of uranium in bismuth was found to range from 2.5×10^{-5} sq cm/sec at 500 C to 4.6×10^{-5} sq cm/sec at 725 C with estimated accuracies of ± 15 percent.

The capillary-bath technique used in the previous studies was employed for measuring the diffusivity of uranium in bismuth. A capillary tube closed at the lower end and containing a known concentration of uranium in bismuth was immersed in a molten bismuth bath. The uranium was allowed to diffuse from the upper open end of the capillary tube into the bath for a predetermined time. The diffusivity value was then calculated from the initial and final concentrations of uranium in the tube and the temperature and duration of the diffusion. The unsteady-state diffusion equation used to correlate the data is

$$\frac{C_0 - \bar{C}}{C_0 - C_s} = 1 - \frac{8}{\pi^2} \left[e^{-\theta} + \frac{1}{9} e^{-9\theta} + \frac{1}{25} e^{-25\theta} + \dots \right], *$$

where

C_0 = initial capillary uranium concentration, weight percent

$\bar{C}$ = final capillary uranium concentration, weight percent

C_s = uranium concentration in the bath, weight percent

$$\theta = \frac{\pi^2}{4} \frac{Dt}{L^2}$$

D = diffusivity, sq cm/sec

L = length of capillary, cm

t = time of diffusion, sec.

The experiments were conducted in a vertical 2 $\frac{1}{2}$ -in.-ID by 24-in.-long stainless steel bomb which was mounted vertically through a 13-in.-long resistance furnace. A recrystallized alumina crucible which contained the melt was positioned inside the bomb. A tantalum holder for the capillary consisted of a vertical support rod and two horizontal arms that were attached to the capillary. The capillary support rod was rotated a few degrees periodically to avoid a localized concentration of uranium at the end of the capillary. A more complete description of the apparatus may be found in ANL-6477, page 69.

The capillary tubes were made of $\frac{3}{16}$ -in.-OD tantalum tubing, having a 0.01-in. wall thickness. To fill the tubes, uranium-bismuth solution was forced by pressurization into a 6-in. length of tubing through a graphite filter frit located at the lower end of the tube. The filled tube

*This equation reduces to: $\frac{C_0 - \bar{C}}{C_0 - C_s} = \left(\frac{4}{\pi} \frac{Dt}{L^2} \right)^{1/2}$ for values of Dt/L^2 less than about 0.25.

was then quickly withdrawn from the melt, cooled, and cut into alternate sections, $\frac{3}{8}$ in. long and one inch long. The one-inch length was faced and used as the capillary tube after a tantalum cap had been force-fitted over one end. The bismuth and uranium in the $\frac{3}{8}$ -in. sections were analyzed to determine the uniformity of the uranium concentration in the one-inch capillary sections.

The results of the experiments are shown in Table 16 and Figure 29. The overall accuracy of the diffusivity values is estimated to be ± 15 percent. The data at 500 C are in good agreement with a value reported by Bonilla¹⁵ of 2.24 sq cm/day (2.59×10^{-5} sq cm/sec) for uranium in bismuth at 500 C. This is the only value for this system found in the literature. The experimental values of diffusivity appear to be lower than would be expected from the Einstein-Stokes equation if 1.421 Å is taken for the radius of the uranium atom. A similar relationship was found between the predicted and experimental values in the uranium-cadmium system (see ANL-6477, page 73) and the uranium-zinc system (see ANL-6569, page 61).

Table 16

DIFFUSION OF URANIUM IN LIQUID BISMUTH,
CAPILLARY-BATH METHOD

Temp (C)	Length ^a of $\frac{3}{16}$ -in.-OD Capillary (cm)	Time (sec $\times 10^{-2}$)	Uranium (w/o)			Computed Values	
			C_0	$\bar{C}$	C_s	Dt/L^2	$D \times 10^5$ (sq cm/sec)
500	2.44	864	0.458	0.163	0	0.340	2.34
500	2.44	864	0.409	0.134	0	0.400	2.54
575	2.43	864	0.404	0.163	0	0.380	2.60
575	2.54	648	0.532	0.220	0	0.270	2.69
650	2.44	648	0.748	0.270	0	0.330	3.03
650	2.44	648	0.561	0.174	0	0.390	3.58
725	2.55	576	0.473	0.134	0	0.430	4.85
725	2.14	576	0.393	0.086	0	0.530	4.21

^aAt run temperature.

¹⁵Bonilla, C. F., Mass Transfer in Molten Metal and Salt Systems, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. IX, P/122, p. 338, United Nations, New York, N.Y. (1956).

Figure 29
DIFFUSIVITY OF URANIUM IN
BISMUTH AS A FUNCTION OF
TEMPERATURE

Measurements of the diffusivity of uranium in liquid aluminum as a function of temperature will complete the measurements of uranium diffusivity. The liquid metals employed in these studies (cadmium, zinc, bismuth, and aluminum) are frequently used as solvents for uranium. A diffusivity measurement in cadmium was made to permit correlation of mass transfer data now being obtained for the dissolution of uranium in cadmium. The measurements were extended to the other liquid metal systems because of the virtual absence of data on uranium diffusivity in these systems and also to expose possible trends or correlations of uranium diffusivities with solvent metal properties.

3. Reactor Materials (R. K. Steunenber)

Pyrometallurgical procedures offer considerable promise as simple, economical methods for producing nuclear fuel materials. Refractory compounds of interest as high-performance reactor fuels can be synthesized by adding carbon, silicon, or other elements to liquid metal solutions of the actinide metals. The product precipitates from the solution and is recovered by suitable phase-separation and retorting techniques. For the preparation of metallic fuel materials an effective method is the direct reduction of actinide oxides, chlorides, or fluorides suspended in a molten halide flux by liquid metal solutions containing magnesium. The present work is concerned with the production of thorium metal directly from the oxide.

Reduction of Thorium Dioxide

(A. V. Hariharan,* J. B. Knighton)

The objective of this program is to develop a practical method for the direct reduction of thorium dioxide to the metal by means of the

Figure 30

EFFECT OF FLUX COMPOSITION ON THE REDUCTION OF THORIUM DIOXIDE

Flux: $\text{CaCl}_2\text{-MgCl}_2\text{-CaF}_2$
 Time: 4 hr or less
 Temperature: 750 C
 Mixing Rate: 800 rpm
 Metal Phase: 300 g Zn-5 w/o Mg.
 Thorium Conc. in Metal Phase at Complete Reduction: 1 w, o

liquid metal-flux technique. In previous investigations (see ANL-6543, page 46) of the effect of flux composition on the reduction of thorium dioxide by zinc-five weight percent magnesium in air atmosphere, some difficulty was experienced with lowered yields and erratic results. The use of tantalum equipment and an argon atmosphere (see ANL-6569, page 66) eliminated these inconsistencies, and the effect of flux composition on the reduction was redefined within the modified conditions. The result is a considerably larger range of composition in the calcium chloride-magnesium chloride-calcium fluoride system in which satisfactory reduction occurs (see Figure 30). Complete reduction in 4 hr at 750 C by zinc-5 weight percent magnesium is achieved in the region enclosed by Curve A in an air atmosphere and in the region enclosed by Curve B in an argon atmosphere. At complete reduction, the thorium concentration in the metal phase was 1.0 weight percent. At the optimum concentration of fluoride anion of about 10 atom percent, over 50 atom percent magnesium cation is required for complete reduction in an air atmosphere, whereas only about 10 or 11 atom percent magnesium cation is needed in an argon atmosphere. Fluxes containing a larger proportion of magnesium cation (and correspondingly lower melting points) result in faster reduction rates, with complete reduction

occurring in two hours in some cases. The points shown in Figure 30 represent a series of confirmatory experiments in which complete reduction was obtained within 4 hr, with various flux compositions.

*Affiliate, International Institute of Nuclear Science and Engineering.

The effects of other variables, such as temperature and mixing rate of the metal and flux phases, have been investigated briefly. For this purpose, a flux composed of 75 mole percent calcium chloride-15 mole percent magnesium chloride-10 mole percent calcium fluoride was selected. Figure 31 shows the effect of the mixing rate on the reduction. Six hundred grams of zinc-five weight percent magnesium alloy and 300 g of the flux containing 6.83 g of thorium dioxide were mixed together in a baffled $2\frac{5}{8}$ -in.-ID tantalum crucible with a straight tantalum paddle, $1\frac{1}{2}$ in. long, $\frac{3}{4}$ in. wide, and 50 mils thick. In all of the experiments, the stirrer was well immersed in the metal phase, being about $\frac{1}{8}$ to $\frac{3}{16}$ in. from the crucible bottom. For the scale and configuration of this equipment, it was found that mixing speeds greater than 700 rpm were necessary to produce sufficient agitation for complete reduction in 4 hr at 750 C.

Figure 31

EFFECT OF MIXING RATE ON THE PERCENT OF THORIUM DIOXIDE REDUCED

Zinc: 570 g } 600 g alloy
 Magnesium: 30 g }
 Flux: 300 g CaCl_2 - MgCl_2 - CaF_2 (75-15-10 m/o)
 ThO_2 : 6.83 g (to give a 1.0 w/o alloy on complete reduction)
 Temperature: 750 C
 Crucible: Tantalum, with baffles
 Agitator: Tantalum paddle, 1-1/2 in. x 3/4 in. x 50 mils; 1/8 to 3/16 in. from bottom of crucible.
 Atmosphere: Argon

The effect of temperature on the reduction rate is shown in Figure 32, where the percent reduction is plotted against temperature for different time intervals and for two different amounts of thorium dioxide. The higher temperatures result in faster reduction rates.

Figure 32

EFFECT OF TEMPERATURE ON THE REDUCTION OF THORIUM DIOXIDE

Zinc: 570 g } 600 g alloy
 Magnesium: 30 g }
 Flux: 300 g CaCl_2 - MgCl_2 - CaF_2 (75-15-10 m/o)
 Crucible: Tantalum, with baffles
 Agitator: Tantalum paddle
 Mixing Rate: 800 rpm
 Atmosphere: Argon

A determination of the approximate melting points of the system calcium chloride-magnesium chloride-calcium fluoride has been made in the composition range of interest. An investigation of the amount of thorium that can be accommodated by the system while maintaining satisfactory reduction rates is also in progress. Other variables which will be examined include the minimum amount of flux and magnesium concentration (in zinc) necessary for reduction, and a few larger-scale experiments to demonstrate the process, and to evaluate the yield and purity of the product.

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. A Laboratory and Service Building has also been constructed. Melt refining, liquid metal extraction, and processes involving fractional crystallization from liquid metal systems are methods which are 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
(E. J. Petkus, H. L. Stethers)

The construction of the EBR-II Fuel Cycle Facility building is essentially complete. However, considerable work is still necessary to correct fabrication and construction deficiencies. This work is being done by the J. F. Pritchard Company under a cost-plus-fixed-fee contract.

A large number of shut-off valves exhibited excessive seat leakage, and a large number of control valves were excessively oversized. In each case, the valve installed was selected by the construction contractor as a substitute for the valve suggested in the contract specifications. The valve manufacturer and the Idaho Operations Office of the AEC have been advised of these deficiencies in an attempt to determine financial responsibility for the necessary repairs or replacement.

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

One 5-ton crane is installed in the Air Cell, and two cranes are installed in the Argon Cell. The Air Cell crane and one of the Argon Cell cranes are in operation. The designs of these cranes are essentially the same except that the movement of the crane bridge in the Air Cell is

rectilinear whereas the movement of each bridge in the Argon Cell is radial about a center pivot. During testing of the cranes, several difficulties were encountered with the crane gears and electrical equipment.

Sliding electrical collector assemblies on crane trolleys supply power to the trolleys from bus bars mounted on the crane bridges. The collector brushes are spring-loaded, and each brush is guided by two pins. Despite the machining of the sliding electrical assemblies to make them conform to drawings (see ANL-6569, page 68), the assemblies did not line up properly with the round bus bars. As a result, a bending strain caused several of the ceramic insulators on the collectors to break. A template was made and used to check alignment and spacing of the rails, trolley wheels, and bus bars. Large variations were observed. As a temporary measure, the diameter of the pin for one sliding collector assembly on the trolley in the Air Cell was reduced by $\frac{1}{32}$ in., and the thickness of the bus bar spacers on the Argon Cell crane was reduced to $\frac{1}{2}$ in. The sliding collector assemblies on these two pieces of equipment now move freely. Alignment, however, is far from satisfactory. The angle clips supporting the bus bars are too close to the sliding contacts and might interfere with the movement of the contacts after the contacts wear. The bus bars are all about $\frac{1}{8}$ in. higher than the sliding collector assemblies, and thereby cause the latter to ride tilted upward. Individual spacing of bus bars is also poor. It is evident that another method for supporting and aligning the bus bars must be found.

After 5 hr of operation of the bridge-drive motor on one Argon Cell crane, one bridge reducer has failed and another is near failure. The cast iron ring gears in these reducers have been completely worn out. The reasons for this gear failure are not completely understood. New gear rings have been ordered. The gears of the other Argon Cell crane show considerable wear after 3 hr of operation. The gear reducer for the bridge in the Air Cell was very noisy because of poor meshing of the high-speed gears, but the cast iron ring gears appeared undamaged after 8 hr of operation. All of these gear-motor units had been poorly assembled, keys had been filed and hammered out of square, snap rings were oversize and loose, motor pinions did not engage properly, bolts were only hand tight, and hammer marks were apparent on gears, keys, and associated items.

The crane rails in the Argon Cell which had been shimmed to meet levelness requirements bowed when the cranes moved over places where there were no shims. To remedy this situation, lead was packed under the rails to fill these spaces. Out-of-level sections of the rail bed for the Air Cell crane are also being leveled.

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

There are two manipulators in the Air Cell and six in the Argon Cell. The designs are basically the same except that the bridge movement in the Air Cell is rectilinear whereas that in the Argon Cell is radial about a center pivot. All of the Argon Cell manipulators are in operation. A number of difficulties have been encountered.

The manipulator rails in the Argon Cell were shimmed to meet levelness requirements. Difficulties were experienced similar to those with the cranes. To overcome these difficulties, molten lead was poured into the space beneath the rails.

Two new arm hoist cables have been installed on a manipulator carriage to replace cables that jammed and broke loose from the hoist drum, probably as a result of abrasion against the edge of the drum covers. The new cables are each one foot longer than the old ones, making it less likely that the cables will slacken on the drums. A way of fastening the cables to the drums so that the cables will not be torn loose is being studied.

During the disassembly of manipulator grip-drive units to permit the replacement of friction disc clutches with magnetic particle drive clutches, scored drive shafts and dry bearings were found. New shafts and bearings were installed, and the drives appear to function satisfactorily.

One of the tapered pins in the telescoping spline tubes fell out. It was actually smaller by 2 to 3 mils than the hole. These pins secure the splines to the tubes and are supposed to be driven in place and staked. They will all be carefully checked.

Several of the carriage and bridge drives for manipulators did not operate properly. The solenoid plungers for the clutches had a tendency to bind, the drive ends of the clutches were off-center to the driven ends, and guide pins would bind. A careful check of three carriage drives and one bridge drive revealed that critical dimensions were not within tolerances. To make sure that the drives are truly interchangeable and that the motors are easily replaceable, it appears necessary to make dimensional checks of every drive assembly and every box in which the drives fit. Special templates have been prepared by the manipulator manufacturer to facilitate these measurements. Corrective action is being deferred until these measurements are made.

These and similar problems are being studied and discussed with the manipulator manufacturer to determine the proper corrective measures and to establish financial responsibility.

d. Cell Viewing and Lighting
(T. Eckels)

Most of the operations performed in the Air and Argon Cells will be viewed through windows installed in 5-ft-thick shielding walls. The windows for the Air Cell are essentially the same as those for the Argon Cell except that the latter have an argon-pressurized inner seal to minimize air inleakage. The basic components of each window are an oil-filled tank unit containing four 9-in.-thick glass panes, a 9-in.-thick single pane in a frame which is closely fitted into a mated niche, and a 9-in.-thick single pane installed in a hinged frame. The tank unit is installed on the operator's side of the cell wall, whereas the hinged pane is at the cell side of the wall. Should the light transmission of the glass in the hinged pane significantly decrease due to radiation darkening, this hinged assembly may be remotely removed and replaced by means of a cell crane and manipulator. Should the other single pane darken, it may also be remotely removed and replaced; however, in this case a special jig must be used. During these operations the tank unit would continue to provide a seal and adequate shielding.

Installation of the 31 windows in the Air and Argon Cells has been completed. The two removable glass panes on each window were remotely installed by means of cranes and manipulators.

e. Installation of Process Equipment
(A. Chilenskas, E. Petkus, M. Slawewski, H. Stethers)

Melt refining will be the first process used in the Fuel Cycle Facility for the reprocessing of fuel discharged from the EBR-II reactor. One of the two melt refining furnaces for the Argon Cell, as well as an associated ingot-removal and sampling device, have been successfully installed by operating personnel using remote means. All of the equipment for the Air Cell and Argon Cell has been designed to be remotely installed and serviced by the use of manipulators and cranes.

Most of the area under the Argon Cell is available for the installation of equipment; this area, the subcell, is bounded by 2-ft-thick concrete walls and contains such equipment as valves, pumps, and motors. Such equipment either would take up valuable space unnecessarily if installed in the Argon Cell or would not be suitable for use in the high radiation field and argon atmosphere. About 90 percent of the subcell equipment has been installed and is now being leak tested and electrically checked.

f. Cell Transfer Locks
(G. Bernstein, A. Chilenskas)

Material transfers into and out of the Argon Cell will be through transfer locks. Two small transfer locks penetrate the wall between the Air Cell and Argon Cell, and a large transfer lock penetrates the floor of the Argon Cell and connects to the Air Cell through a Transfer Cell (see ANL-6569, page 70).

Installation and testing of transfer lock equipment is continuing. The leaks and defects in the welds and gasket surfaces of the end fittings for the small transfer locks have been repaired and the fittings have been bolted into place. Some difficulty has been noted in the movement of loaded carts in the small locks due to flexing of the rails on which the carts ride. The rails will be stiffened and given additional support to eliminate this problem. The locking mechanism for the transfer lock lids is being modified to permit remote adjustment to compensate for gasket compression.

The hinged lid of the large transfer lock did not operate satisfactorily because guide bars did not give the lid adequate support in all positions of its travel. Larger support pins are being installed, and a guide plate is being designed to replace the guide bars which gave insufficient support.

The main sealing platform on the bottom of the large transfer lock was improperly finished. The seal surface was refinished by the vendor and has been reinstalled prior to operational testing.

Transfer Cell equipment used to move material from an opening in the Air Cell floor to the large transfer lock of the Argon Cell includes a platform to carry materials, a transfer cart to position the platform beneath either cell opening, and a hydraulic ram beneath each cell opening to elevate the platform. This equipment has been installed and is being tested. The equipment generally performs satisfactorily, but changes have been necessary in limit switches, the hydraulic control system, and the cart drive.

g. Miscellaneous Cell Service Equipment
(M. Slaweki)

There are 65 Argon Cell service sleeves in which feed throughs may be installed to provide piped and electrical services to the in-cell equipment (see ANL-6569, page 71). The feed throughs are sealed in 5-ft-long sleeves, approximately 6 in. in diameter, which are cast in 4 ft of concrete in the Argon Cell floor. Two types of electrical feed

throughs provide either 1 or 48 electrical leads, and three types of piping feed throughs provide one, two, or eight piped services. Forty-five service feed throughs and twenty blank feed throughs have been installed remotely, and tests show that the installations meet leak-tightness requirements. Examination of the electrical and thermocouple feed throughs revealed a vendor error in the fabrication of the slot guides. The guides are used for locating purposes when inserting electrical or thermocouple plugs into the receptacles on the top of the feed throughs. The slot guides were removed from the feed throughs and shipped to the vendor for necessary repairs.

2. Development of Service Equipment

a. Interbuilding Fuel-transfer Coffins (G. Bernstein, A. Chilenskas)

Fuel subassemblies containing spent or reconstituted fuel will be transferred between the reactor and the Air Cell of the Fuel Cycle Facility in 20-ton interbuilding fuel-transfer coffins. Two types of interbuilding coffins will be fabricated (see ANL-6569, page 71). One coffin is now being fabricated by O. G. Kelley and Company and is scheduled for delivery in Idaho on September 16, 1962. The second coffin is being designed at Argonne National Laboratory. The design is nearly complete and several components are currently being fabricated.

When a spent fuel subassembly is loaded into a coffin, the subassembly will have a thin coating of sodium which must be removed before the subassembly is moved into the Air Cell. A sodium-removal station is to be located in the passageway between the reactor building and Fuel Cycle Facility. This station will provide services to the subassembly coffins for the in situ removal of the sodium film. Waste-monitoring and waste-disposal equipment will also be provided.

The proposed sodium-removal scheme consists of converting the sodium to sodium hydroxide by adding oxygen and water vapor to the inert coolant gas circulating within the coffin and subsequently removing the sodium hydroxide by a wash of liquid water. The chemical conversion is to occur in two steps. First, the sodium is to be converted to the oxide by the addition of a small flow of air to the recirculating coolant gas, with any pressure buildup relieved through a bleed to the suspect stack. In the second step, the oxide is to be converted to the hydroxide by the addition of humidified air. The sodium hydroxide film is to be removed by a once-through water wash, and the subassembly is to be dried by once-through air.

Calculations have been made in order to determine values of parameters for this sodium-removal procedure. The calculations, for which it was assumed that there will be a 100-g holdup of sodium in the

subassembly, show that about 30 min must be allowed for sodium-to-sodium hydroxide conversion if an average heat generation of one kilowatt is to be maintained. It is desirable to limit the chemical heat load to about this value to prevent fuel pins from becoming excessively hot. In practice, the reaction rate will be controlled by limiting the concentration of oxygen and water vapor added to the recirculating coolant gas while monitoring the temperature of the gas leaving the subassembly. The required addition rate for air will be about 0.4 cfm, and the addition rate for humidified air which has been 80 percent saturated at 70 F will be about 7 cfm. The water wash will be limited to about 25 gal, and the system will be designed to deliver about 5 gal/min.

Two small-scale experiments have been performed in a Pyrex glass reaction tube, each on a 4.5-in. section of a dummy stainless steel EBR-II fuel pin (all wetted surfaces of the subassembly will be stainless steel). Each pin was coated with about 0.2 g of sodium, and each experiment used similar process conditions and had similar results. Single-pass nitrogen flowing past the pin at a linear rate of about 46 ft/sec was used to simulate the coolant flow. During the first 15 min of each experiment, air was added to the nitrogen to give a concentration of about 0.2 percent oxygen. The pin was held at a temperature of about 110 C. Under these conditions, the sodium film was observed to turn a dull grey, indicating the formation of a suboxide. After nitrogen having a moisture content of 0.5 to 1.0 percent was substituted for air, the reaction was continued for 15 min more, during which time the film was observed to gradually turn white. The film formed during the first two steps remained substantially adherent to the pin, but some particles were observed to be blown loose by the gas. Water was then allowed to flow past the pin, and the visible film was removed in the first few seconds, leaving the pin bright and shiny. However, examination of the pin after the experiment when it had been exposed to air showed that the pin had developed a thin, slick film of sodium hydroxide - evidently from sodium retained by the stainless steel pin. Analysis of gas samples taken during the various steps indicated that no more than a trace of hydrogen was produced by the reactions.

The design of a sodium-removal station based upon these calculations and experiments is underway. It is anticipated that further development of procedures will be necessary. When subassembly coffins become available, additional work is to be done at the EBR-II site with sodium-coated, unirradiated, full-scale subassemblies.

b. Viewing and Lighting
(T. Eckels)

One thousand-watt mercury vapor lamps with white phosphor-coated soft-glass envelopes are used to illuminate the Argon and Air Cells (see ANL-6287, page 82). Satisfactory viewing of the work

within these cells will depend primarily upon a high-enough level of "effective illumination," which is defined as the product of the in-cell illumination and the window transmittance. The initial in-cell illumination (250 ft-candles) was measured at the Fuel Cycle Facility, and the initial effective illumination, at a location where visibility is poorest in the Argon Cell (midway between the central control room wall and the operating annulus wall), was calculated to be 35 foot-candles* (window transmittance was 0.14).

From laboratory-scale experiments, the effects of gamma radiation on the light transmittance of the shielding windows and upon the lumen output of the 1000-w lamps have been estimated. Actual service experience and additional experiments now permit estimates of three additional variables whose effects upon the effective illumination must be considered. These variables are lamp life, lamp voltage, and ambient temperature.

A mockup lighting installation (see ANL-5996, page 36) which has been in service for $3\frac{1}{2}$ yr has been a source of data on lamp life.

Figure 33

LIGHT OUTPUT OF LAMPS AFTER VARIOUS PERIODS OF USAGE

1000-w White, Fluorescent, Mercury Vapor Lamps Tested in Mockup Fuel Cycle Facility.

Seven of the nine original lamps are still in service. Figure 33 is a bar graph showing the number of hours of operation and the present relative light output of the nine lamps currently in use. Two fixtures each had their lamp replaced twice, and the lamp in a third fixture was little used. Two of the replaced lamps burned out after approximately 300 hr of service each, and the other two replaced lamps were still operating when removed for reasons not related to the experiment. A rough graphical integration, which takes into account a rather rapid deterior-

ation of lumen output to about 80 percent of the initial rating during the first 1,000 hr of operation (observed in a different experiment utilizing five other lamps), indicates the mean lumen/hour output during 6,000 hr to be 70 percent of the initial lumen/hour rating. This will be acceptable in the process cells of the Fuel Cycle Facility.

* $Ill_{eff} = 250 \text{ ft-candles} \times 0.14 = 35 \text{ ft-candles}$

A lighting installation which has been in use for over 2 yr and which has yielded interesting information is that in the Senior Cave in the Chemical Engineering Building at Argonne. The Senior Cave is a complex of three gamma hot cells, two of which have been operated at a maximum of 6,000 c of 1-Mev gammas and the other at a maximum of 10 c. The lighting for the three cells is furnished by sixteen 400-w white, fluorescent, mercury vapor lamps. The effective illumination at the time of commissioning was 56 ft-candles.* One lamp in each cell is operated 24 hr/day. Two of the three continuously energized lamps have each given 17,000 hr of service. The remaining 13 lamps have been operated 8 hr each working day. Twelve now have 3,500 hr of operating time. The thirteenth lamp failed to start at 300 hr; its successor now has 3,200 hr of operating time. The operators report no noticeable change in viewing ability, although the present effective illumination is estimated to be approximately 45 ft-candles.

Experiments have been carried out to determine the effect of variation in line voltage and ambient air temperature on the light output of two types of 1,000-w mercury vapor lamps. Results indicated that the expected temperature of 40 C in the two Fuel Cycle Facility cells (15 C above the usual 25 C of the mockup) should cause no more than a 10 percent decrease in the cell illumination of the Argon and Air Cells. A line voltage variation of 1 percent should affect the illumination by no more than 2 percent.

c. Materials Testing
(G. Bernstein, A. Chilenskis)

Evaluation of several elastomers as possible substitutes for the lead gasket now specified for the large transfer lock has been completed. Three elastomers, Neoprene, gum rubber, and Adiprene C,** were irradiated while under compression in a test assembly (see ANL-6477, page 76). Adiprene C was found to be resilient after an exposure of 3×10^9 rad and was judged to be serviceable to this level. As previously reported, Neoprene and gum rubber were found to be serviceable to levels of 2×10^8 rad and 4×10^8 rad. For the intended use, Adiprene C is considered satisfactory and no further testing will be carried out.

* $Ill_{eff} = 280 \text{ ft-candles} \times 0.20 = 56 \text{ ft-candles}.$

**A product of Minnesota Rubber Co.

3. Development of Process Equipment

a. Skull-oxidation Equipment

(W. E. Miller, M. A. Slaweck, H. Stethers)

After the melt refining step is carried out, a skull remains in the zirconia crucible. This skull contains significant quantities of fissionable material which will be recovered by means of the skull reclamation process. In order to remove the skull from the crucible, the skull will be oxidized to a powder and the powder transferred to an oxide-storage container. Equipment for the skull oxidation step and for the transfer of the oxide powder is being developed.

To accumulate operating experience, the prototype skull-oxidation furnace has been in use for 516 hr. (The oxidation furnace is described in ANL-6477, page 87, and the gas-control system for the furnace is described in ANL-6543, page 85.) About 40 kg of skull material and uranium-fission alloy scrap has been oxidized during this period. This is equivalent to oxidizing about 80 skulls from plant-scale melt refining runs of 95 percent yield. The original furnace heater is still operating satisfactorily.

The skull oxidation furnace, an oxygen-removal unit, and associated gas-control equipment will be combined into an integrated operating unit and tested at Argonne. The design of a remotely rechargeable oxygen-removal unit, which will use a heated copper bed to remove oxygen from the gas discharged from the oxidation furnace, has been completed. Drawings and wiring diagrams for the control panel board and control system have also been completed. Installation of the operating unit is expected to be completed during the next quarter.

b. Collection of Metal Vapors

(W. E. Miller)

The product from the precipitation step of the skull reclamation process is uranium coated with magnesium-zinc. Distillation is a convenient means of removing the magnesium-zinc coating from the uranium. If possible, the melt refining furnace will be adapted for this distillation. The main problem in this approach is the design of a condenser to collect the distillate.

Two condenser designs have been tested recently in the melt refining furnace. The first condenser design consisted of a thin-walled stainless steel cylinder (the condenser) mounted vertically on an insulated furnace cover which in turn rested on the furnace rim. This arrangement, however, permitted the metal vapors to contact a zirconia

brick ring at the top of the furnace. After one distillation in which a 700-g magnesium charge was used, considerable distilled metal was found deposited in the zirconia brick ring and in insulation between the susceptor and the furnace wall. This design was abandoned since such deposits would impair proper operation of the furnace.

Figure 34

MELT REFINING EQUIPMENT WITH GRAPHITE CONDENSER

The second condenser design consisted of the arrangement shown in Figure 34. The graphite condenser rested directly on the gasketed lip of the crucible to minimize the escape of metal vapors. More promising results have been obtained in distillations with this arrangement. In one distillation in which 88 percent of a 420-g charge of 50 weight percent magnesium-zinc was distilled, 89 percent of the distillate was recovered in the condenser and most of the remainder was deposited on the Fiberfrax insulator. In the next distillation, the charge was doubled (800 g), and essentially the same percent recovery was obtained. At

the end of each run, the condenser and crucible were found to be bonded at the Fiberfrax gasket. Such bonding would hinder remote disassembly of the equipment. Alternative gasket materials have been ordered for testing.

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

The first model of a skull oxide-processing furnace has been received and is being installed in the EBR-II mockup area at Argonne for test purposes.

A crucible charger will be used to dump skull oxide into the crucible of the skull oxide-processing furnace. One crucible charger has been built and tested. The initial operation was satisfactory, but dust accumulated in the mechanism after a period of operation and made the operation of the unit erratic. Some minor changes will be required to eliminate this problem.

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

The skull reclamation process requires the heating and mixing of molten metal-salt systems at temperatures up to about 800 C. Although conventional mixing and heating methods have been found satisfactory for the demonstration of the process on a small scale, the use of low-frequency inductive power to provide both heating and mixing of the charge is being investigated. Vigorous movement of a molten metal charge

Figure 35
FLOW PATTERN DURING
INDUCTIVE MIXING

can be caused by inducing currents to flow within the charge by an externally wound induction coil. The flow pattern¹⁶ commonly ascribed to this type of mixing is shown in Figure 35. Appreciable simplification of plant equipment is anticipated if inductive heating and mixing should prove feasible.

In this investigation of the adequacy of low-frequency power for process mixing and heating, information is being developed regarding power requirements, insulating materials, design and performance of un-cooled copper coils, and the trapping of vapors on a plant scale (5 kg of skull oxide). The

experimental work on the metal-salt systems has taken place in a closed furnace to which a gas-recirculation system has been added. Argon has been used as the blanket gas. A carbon vane, dry-air pump* is used to circulate the gas through a filter-sorber bed. The filter consists of three layers of $\frac{1}{8}$ -in. bonded fiberglass (American Air Filter Company, Air Mat. No. 12), and the sorber is a bed of Molecular Sieves,** type 5A. This system has been successful in keeping the furnace atmosphere clean when zinc-Dow 230[†] flux systems are used so that visibility through the furnace window has remained unimpaired through the run. The inside of the furnace has remained free of deposited vapors, except for a thin film of a varnish-like deposit which is believed to be a vaporized constituent originating from the graphite crucibles. The gas pump has been run without failure for about 60 hr. Measurement of the gas flow after 60 hr of use shows that the pumping capacity has remained nearly constant at 6 scfm.

¹⁶Paschkis, V., and Persson, J., Industrial Electric Furnaces and Appliances, Interscience Publishers, Inc., New York (1960) p. 524.

*Model 50DA2DF, manufactured by M. D. Blowers, Inc.

**A product of the Union Carbide Corporation.

[†]A flux manufactured by the Dow Chemical Company. The flux contains 55 percent KCl, 34 percent MgCl₂, 9 percent BaCl₂, and 2 percent CaF₂.

The mixing obtained inductively is being examined by two experimental methods. One method is by means of visual observation of zinc and zinc-salt systems heated just above the melting temperature of the salt. The second method is to follow the reduction of skull oxide by a zinc-magnesium-salt system heated and mixed inductively. The extent of the reduction is calculated from a uranium analysis of a sample of the zinc-magnesium phase.

An experiment (IM-8) has been completed in which the agitation obtained for a zinc and a zinc-Dow 230 system was observed as a function of power input to the system. A convenient index of the vigor of agitation is the height to which the center of the charge surface rises with reference to its edge. This rise is often referred to as "lift" (see Figure 35). The lift was determined by measuring distances A and B as shown on Figure 35 with the furnace top removed. The zinc temperature during these measurements was kept slightly above its melting point.

A plot of lift as a function of total power input for a zinc charge is shown in Figure 36, which also presents charge geometry and

Figure 36

INDUCTIVE MIXING: VIGOR OF AGITATION AS A
FUNCTION OF POWER INPUT

charge data. As shown by the plot, a lift of about 2 in. was obtained for a power input of about 10 kw. Visual observation of the metal surface at this power input showed that the metal phase was undergoing extremely vigorous agitation. This experiment was continued by observing the action of the zinc phase after small incremental additions of Dow 230 flux with the power at 10 kw. Vigorous movement of the salt could be observed after each incremental addition until sufficient salt was added to

form a layer $1\frac{1}{2}$ in. thick under quiescent conditions. With this amount of salt, the metal no longer broke through the surface at the center of the molten salt layer, although considerable movement of small particles in the salt was visible. Although no firm conclusion can be drawn regarding the adequacy of mixing from these observations, they show that inductive agitation of metal-salt systems does occur. It is anticipated that, with proper selection of the power supply and proper system design, adequate mixing is possible for the noble metal-extraction step and the reduction step of the skull reclamation process.

Experimental work with low-frequency power-supply systems has been continued. Recently, a capacitor bank was added to provide for power-factor correction. A block diagram of the power supply system

now in use is shown in Figure 37. This supply system was used in Run IM-6 (see Figure 38). With the charge at 800 C, the power at the 36 KVA transformer primary (see Figure 37) was about 15 kw with a power factor of about 0.96. The voltage and current were also measured on the secondary side (load) of the transformer. Assuming a 1-kw power loss in the transformer, the power factor was about 0.4 for a measured KVA of 34.

Figure 37

INDUCTIVE MIXING: SIXTY-CYCLE POWER SUPPLY SYSTEM

Figure 38

APPARATUS FOR REDUCTION OF SKULL OXIDE Run IM-6

Charge

Zinc, 231 lb
Magnesium, 11.5 lb
Skull Oxide, 9.7 lb
Dow-230 Flux, 24.3 lb

Coil

Copper bar, 1 in. x 1/2 in., 1/8-in. spacing, 24 turns total, electrically connected at 17th turn, 14 in. ID x 16 in. OD

Power

60 cycle

Crucible Insulation

Fiberfrax sheeting

As may be seen from Figure 39, about 6 hr were required to heat a plant-size charge of zinc (231 lb) to an operating temperature of 800 C. The induction coil was cooled by radiation and convection to the furnace walls, and operated at less than 600 C. It is anticipated that shorter heatup times will be possible with the larger power-supply system now being procured. This run demonstrates the feasibility of using a 60-cycle supply system to provide the necessary power for heating plant-scale charges in the skull reclamation process.

Figure 39
INDUCTIVE MIXING: HEATUP CURVE FOR
RUN IM-6

In Runs IM-6 and IM-9, the reduction of skull oxide by a Dow flux-magnesium-zinc system held at 800 C was attempted. The heating and mixing were accomplished by an induction coil operating with a 60-cycle, low-voltage, high-amperage power supply. Analytical results show a 12 percent reduction for Run IM-6 and a 40 percent reduction for Run IM-9.

The geometry and charge data for Run IM-6 are shown on Figure 38. The geometry and charge data for Run IM-9 are shown on Figure 40.

The skull oxide charges were sized to give a uranium concentration in the metal phase of about 3.5 weight percent for a 100 percent reduction. At 800 C the metal phase can dissolve five weight percent uranium (see ANL-6477, page 93). The final sample for each run was taken after the charge had been held for 2 hr at about 800 C. The power input during the 2-hr period was 15 kw in Run IM-6 and 9 kw in Run IM-9. The improvement in the reduction obtained in Run IM-9 (40 percent reduction) over Run IM-6 (12 percent reduction) is believed to be due to the more vigorous agitation achieved during this run; however, it is recognized that other factors could have been controlling in the rate of reduction observed. Further work is planned in which tests will be performed with higher rates of power input (and hence more vigorous agitation). These higher power inputs will be made possible by the use of improved coils and larger power-supply equipment.

Figure 40
APPARATUS FOR REDUCTION OF SKULL OXIDE
Run IM-9

Charge: Zinc, 78.6 lb; Magnesium 3.9 lb; Skull Oxide 3.9 lb;
Dow-230 Flux 12 lb.

Coil: Copper bar, 1 in. x 1/2 in., total turns 24, tapped at
17th turn, water cooled, 12 in. OD x 10 in. ID, spaced 1/8 in.
between turns.

Power: 60 cycle

Crucible Insulation: Fiberfrax sheet

C. Chemistry of Liquid Metals (I. Johnson, 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 re-processing of nuclear fuels. The results of these studies also provide ideas and data for the formulation and testing of theories of liquid metal solutions.

1. Solubilities in Liquid Metals

Of prime importance in the practical design of fuel-reprocessing methods 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. Since the solubility and temperature coefficient of solubility of a metallic phase in a liquid metal solvent are dependent on the interatomic forces operative in the solution, systematic studies may lead to a greater insight of the nature of these forces and their variation with the basic properties of the solute and solvent atoms. For such fundamental applications, it is necessary to know the constitution of the solid phase in equilibrium with the saturated liquid phase.

Solubility of Strontium in Liquid Zinc (I. Johnson, K. E. Anderson, and J. Bartos*)

The solubility of strontium in liquid zinc has been measured by analyzing filtered samples of the liquid phase in equilibrium with the strontium-zinc intermetallic phase. Two different experiments have been completed. The first experiment established the solubility above 600 C and indicated that the solubility below 600 C would require an analytical method more sensitive than the flame photometric method used in the first experiment. Consequently, a radiochemical analytical method using strontium-85, prepared by neutron irradiation of strontium metal, was used in the second experiment. Three samples taken at 587, 628, and 666 C from the second experiment were analyzed by the flame photometric method to determine the specific activity of the strontium. This method of determining the specific activity avoided the errors introduced by partial oxidation of the strontium metal by air during irradiation and dissolution in the molten zinc. The results of the two experiments are given in Table 17 and shown in Figure 41. The data obtained above 506 C may be represented by the equation

$$\text{Strontium: } \log (\text{atom percent}) = 9.619 - 9940 T^{-1} .$$

This equation is represented by the straight line in Figure 41. The data

*Co-op Student from Illinois Institute of Technology.

Table 17

SOLUBILITY OF STRONTIUM IN LIQUID ZINC

Experiment	Temperature (C)	Solubility of Strontium (w/o)	
		Flame Photometric	Radiochemical
A	727	0.78	
A	692	0.29 ₉	
A	642	0.073	
A	604	0.018 ₅	
B	666	0.13 ₀	0.13 ₁
B	628	0.055	0.058
B	587	0.013 ₈	0.013 ₁
B	545		0.0043
B	529		0.0025 ₀
B	506		0.0010 ₆
B	468		0.00091
B	447		0.00067
B	433		0.00062
B	428		0.00012 ₅

Figure 41

SOLUBILITY OF STRONTIUM IN LIQUID ZINC

below 506 C are seen to deviate significantly from this equation. The concentration of impurities (10 ppm) is of the same order of magnitude as the apparent solubility of strontium at these temperatures and may be a contributing factor to this difference in behavior.

Microscopic examination of the solubility ingot revealed the presence of the intermetallic compound SrZn_{13} , which has the face-centered cubic NaZn_{13} (D_{23}) type of structure. This is presumed to be the phase in equilibrium with the saturated solution.

Solubility of Zirconium in Liquid Magnesium-Zinc Solutions
(I. Johnson, K. E. Anderson)

The solubility of zirconium in nominally 20 and 30 weight percent liquid magnesium-zinc solutions has been measured as a function of temperature. This is a continuation of the study reported in the last quarterly report (see ANL-6569, page 82). The experimental method was the same as used in the previous study. The data are given in Table 18 and shown in Figure 42. The breaks in the solubility curves indicate a change in the composition of the equilibrium solid phase. The equilibrium solid phases have not as yet been isolated from the ingots.

Table 18

SOLUBILITY OF ZIRCONIUM IN MAGNESIUM-ZINC SOLUTIONS

<u>Temp (C)</u>	<u>Solution Composition (w/o)</u>		
	<u>Zinc</u>	<u>Magnesium^a</u>	<u>Zirconium</u>
758	79.3	19.1	1.59
756	78.2	20.2	1.63
718	79.1	19.9	1.05
663	77.8	21.8	0.43
624	76.3	23.5	0.15 ₈
584	78.2	21.8	0.024 ₉
764	71.3	27.8	0.87
718	70.4	28.7	0.76
676	69.9	29.5	0.62
625	70.3	29.4	0.26
597	68.6	31.3	0.11 ₇
562	68.6	31.4	0.036
557	68.6	31.4	0.038
514	68.6	31.4	0.0031
482	65.4	34.6	0.0017

^aMagnesium obtained by difference

Figure 42
SOLUBILITY OF ZIRCONIUM IN
MAGNESIUM-ZINC SOLUTIONS

Zinc-Vanadium System
(M. G. Chasanov, P. D. Hunt)

The solubility of vanadium in liquid zinc has been previously reported along with the results of thermal analysis and X-ray diffraction analysis of zinc-vanadium alloys (see ANL-6477, page 89). The inter-metallic phases present in the system were discussed in ANL-6569, page 91. The results of these thermal, metallographic, X-ray, and solubility studies have been combined to construct the zinc-vanadium phase diagram shown in Figure 43. Three ternary phase equilibria occur:

Mutual solid solubilities in vanadium and zinc appear to be negligible.

Figure 43
THE ZINC-VANADIUM PHASE DIAGRAM

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

Evidence for the existence of a second intermetallic phase, the epsilon phase, in the zinc-uranium system in addition to the delta phase was recently confirmed (see ANL-6569, page 80). This led to renewed efforts to establish the peritectic temperature at which the epsilon phase decomposes to the delta phase and uranium-saturated melt. Thermal analysis measurements made on several alloys had indicated that the peritectic temperature was about 830 C, but the results were not reproducible and were only obtained on heating. Additional measurements have now been made by the differential thermal analysis method with alloys containing 15, 20, and 24 percent uranium at heating and cooling rates in the range 5 to 15 degrees per minute. Weak but reproducible arrests were obtained at 825 to 830 C on heating and 765 to 775 C on cooling.

Some evidence of the peritectic temperature had also been indicated by a break in the liquidus line in the zinc-rich portion of the zinc-uranium system. This line had been established mainly by solubility measurements (see ANL-6333, page 109). However, the data near the peritectic temperature were so erratic that a break in the liquidus line could not be definitely established. Accordingly, new data on liquidus temperatures were obtained in the temperature range from 768 to 862 C by the thermal analysis of stirred melts during heating and cooling. Figure 44

shows the new data coupled with a portion of the data obtained previously. A break in the curve at about 800 C is clearly indicated. Thus it is now clear that the peritectic decomposition temperature of the epsilon phase is about 800 C.

Figure 44
THE ZINC-RICH LIQUIDUS IN THE
ZINC-URANIUM SYSTEM

2. Thermodynamic Studies

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

Studies are underway on the plutonium-zinc system using the galvanic cell method. The effusion method is being used for the systematic study of the light rare earth metal-zinc and light rare earth-cadmium systems. The results for the lanthanum-zinc system are presented below.

Lanthanum-Zinc System (Effusion Studies)
(E. Veleckis, E. Van DeVenter)

The system lanthanum-zinc has been studied by Rolla and Iandelli,¹⁷ who found evidence for the existence of five intermediate compounds: LaZn_{13} , LaZn_8 , LaZn_4 , LaZn_2 , and LaZn . Their composition assignments for the two zinc-rich compounds were in conflict with those of Schramm,¹⁸ who found the phases LaZn_{11} and LaZn_9 instead of LaZn_{13} and LaZn_8 . According to Schramm, LaZn_{11} undergoes a polymorphic transformation at about 710 C. Below this temperature the compound shows a crystalline structure different from that of CeZn_{11} . Two peritectic decompositions at 930 C and 852 C, also found by Schramm, suggested the existence of two additional intermediate phases between ~80 and ~88 atom percent zinc. The first of these phases, which has been identified by X-ray studies,¹⁹ probably corresponds to LaZn_5 .

Figure 45
LANTHANUM-ZINC SYSTEM - EFFUSION
ISOTHERM AT 515 C

In the present work, a recording effusion balance was utilized to clarify the phase relationships in the lanthanum-zinc system. An alloy having a composition LaZn_{14} was prepared by sealing weighed amounts of zinc and carefully abraded lanthanum in a small tantalum crucible which, in turn, was enclosed in a thick-walled, stainless steel container. The alloy was heated for about one hour at a temperature slightly above the melting point of lanthanum. This was followed by a 14-day annealing period at 500 C and a water quench.

A typical effusion isotherm at 515 C is shown in Figure 45, in which the logarithm of the rate (g/sec) of effusion is plotted against the atom ratio of zinc to lanthanum. The isotherm is comprised of a series of descending steps, each step showing rather extensive rounding of corners, which is caused by a lack of equilibrium brought about by the rapidly diminishing surface of the zinc-producing phase just prior to the formation of a new phase. The compositions

¹⁷Rolla, L., and Iandelli, A., *Ricerca sci.*, **20**, 1216 (1941).

¹⁸Schramm, J., *Z. Metallkunde*, **33**, 358 (1941).

¹⁹Nowotny, H., *Z. Metallkunde*, **34**, 247 (1942).

at which the sharpest rate decreases take place correspond to the atom ratios of the pure phases just formed. Horizontal portions after such rate decreases indicate the extent to which these phases are in equilibrium with the succeeding phases.

Six stable intermediate compounds can be distinguished from the inspection of the isotherm: LaZn_{13} , $\text{La}_2\text{Zn}_{17}$, LaZn_7 , $\text{LaZn}_{5.3}$, LaZn_4 , and LaZn_2 . Of these phases, only LaZn_7 shows a solubility range. Also discernible in the isotherm is a small irregularity appearing between LaZn_{13} and $\text{LaZn}_{8.5}$. It suggests the existence of a compound which is relatively unstable with respect to LaZn_{13} . The incomplete crystallization of this compound may be due to the lack of equilibrium in the effusion crucible enhanced by the instability of the phase. It is believed that this phase corresponds to the 1:11 compound, since the known²⁰ patterns of LaZn_{11} were recognized in our diffraction data obtained from samples of that composition (see below).

In order to verify the effusion results, a series of alloys encompassing the complete composition spectrum were submitted for X-ray diffraction analysis. These alloys were prepared in the effusion apparatus by partial evaporation of zinc until an alloy of the desired composition was reached. A comparison of the effusion data with the X-ray data, shown in Figure 46, reveals good agreement between them. As a result of this comparison the following conclusions may be drawn: (1) X-ray patterns denoted by the symbols S, I, and C, which were not identified by the X-ray Diffraction and Spectroscopy Group, appear to correspond to the compounds LaZn_7 , LaZn_4 , and LaZn_2 , respectively, found in the effusion study. (2) The appearance of strong diffraction lines of LaZn_{11} (e.g., in sample $\text{Zn/La} = 10.84$) tends to indicate that the compound is stable under the conditions of the present experiments, even though the effusion data suggest instability of this compound. (3) The similarity of the diffraction patterns obtained for $\text{La}_2\text{Zn}_{17}$ to those of other M_2Zn_{17} compounds confirms its stoichiometry. (4) Effusion results consistently yielded the compound $\text{LaZn}_{5.3}$. X-ray patterns of this compound, however, indicate a hexagonal structure of the CaCu_5 type, thus indicating the compound to be LaZn_5 . This discrepancy has not yet been resolved. (5) Because of the extremely low evaporation rates, the effusion experiment, the results of which are shown in Figure 45, was not carried far enough to identify LaZn . However, the existence of this compound is demonstrated by the results of X-ray analysis of a sample having a zinc to lanthanum atom ratio of 1.30 and from a separate effusion experiment not reported here.

²⁰Sanderson, M. J., and Baenziger, N. C., *Acta Cryst.*, **6**, 627 (1953).

Figure 46

COMPARISON OF EFFUSION AND X-RAY DIFFRACTION^a DATA FOR THE SYSTEM LANTHANUM-ZINC

^aX-ray diffraction data were obtained and interpreted by R. Schablaske and B. Tani of the X-ray Diffraction and Spectroscopy Group.

^bCompositions in atom ratio (Zn/La) units.

^cThe compound "LaZn₁₃" was identified assuming NaZn₁₃ structure.

^dPatterns denoted by "La₂Zn₁₇" are similar to those obtained for delta or epsilon U₂Zn₁₇.

^eAlphabetical symbols (S, I, C) denote unidentified diffraction patterns believed to represent single phases.

^f"LaZn₅" was identified on the basis of calculated interplanar spacings from reported parameters. No powder data available in the literature.

In the current literature,^{21,22} the phase diagram of the lanthanum-zinc system is usually constructed in favor of the results of Schramm.¹⁸ Thus, the compound LaZn₁₃ is replaced by LaZn₁₁ and LaZn₄ by "LaZn₅." The results of the present study demonstrate that all four of these compounds are capable of existence. The questions of the exact stoichiometry of "LaZn₅" and the temperature range in which LaZn₁₁ is stable remain unanswered and require further work.

3. Magnetic Studies of the Uranium-Cadmium Intermetallic Compound UCd₁₁ (F. Cafasso, D. Gruen*)

The magnetic susceptibilities of a number of intermetallic compounds of the type AB₁₁ where A is either a rare earth or actinide

²¹Hansen, M., and Anderko, K., Constitution of Binary Alloys, McGraw-Hill Book Co., New York (1958), p. 895.

²²Gschneidner, K. A., Rare Earth Alloys, D. Van Nostrand Co., Princeton, N. J. (1961), p. 334.

*Cooperating Chemist - Chemistry Division.

element and B is cadmium are being measured* in a joint effort of the Chemical Engineering and Chemistry Divisions.

The magnetic susceptibility of UCd_{11} has been remeasured. Measurements were made with two polycrystalline samples taken from the same UCd_{11} preparation which was used in the preliminary experiments reported earlier.* These measurements differed from the earlier ones in only one way. The quartz ampoules which contained the samples were not sealed with an epoxy cement. In this way, the magnitude of the diamagnetic correction was greatly reduced and the size of each sample could be enlarged. These two factors resulted in improved experimental accuracy.

Molar susceptibilities of the compound UCd_{11} ($M\chi_{\text{UCd}_{11}}$) and of uranium in this compound ($M\chi_{\text{U}}$) calculated from measurements at maximum field strength are tabulated in Table 19 for both samples. In Figure 47 these data are shown plotted as the reciprocal molar susceptibility of uranium ($M\chi_{\text{U}}^{-1}$) against the absolute temperature. From 4.2 K to room temperature, the susceptibility obeys a Curie-Weiss law,

$$\chi = \frac{C}{T - \Delta},$$

with $C = 1.77_8$ and $\Delta = -41.2$ K.

Table 19

MOLAR MAGNETIC SUSCEPTIBILITY OF UCd_{11} ^a

Temp (K)	Sample I			Sample II		
	$M\chi_{\text{UCd}_{11}} \times 10^3$	$M\chi_{\text{U}} \times 10^3$	$M\chi_{\text{U}}^{-1} \times 10^{-2}$	$M\chi_{\text{UCd}_{11}} \times 10^3$	$M\chi_{\text{U}} \times 10^3$	$M\chi_{\text{U}}^{-1} \times 10^{-2}$
296.2	5.06	5.28	1.89			
294.6	-	-	-	5.07	5.29	1.88 ₈
77.2	14.8 ₃	15.0 ₅	0.66 ₄	14.7 ₇	14.9 ₉	0.66 ₇
63.2	16.9 ₄	17.1 ₆	0.58 ₃	-	-	-
4.2	38.76	38.98	0.25 ₇	38.5 ₆	38.7 ₈	0.25 ₇
2.3	-	-	-	39.3 ₇	39.5 ₉	0.25 ₃

^aCalculated from measurements made at maximum field strength.

Below 4.2 K, the susceptibility appears to become essentially independent of temperature. This behavior in a magnetically dilute system is indicative of a nondegenerate ground state of the magnetic electrons and can occur only for an even number of such electrons.

*Measurements for CeCd_{11} may be found in ANL-6287, page 118; for NdCd_{11} in ANL-6333, page 118. Preliminary results for UCd_{11} may be found in ANL-6379, page 124.

Figure 47
TEMPERATURE VARIATION OF
RECIPROCAL MOLAR SUSCEP-
TIBILITY OF URANIUM IN
 UCd_{11}

From the Curie constant, a magnetic moment of 3.78 Bohr magnetons is calculated. The magnetic moment of a $5f^2$ configuration is calculated to be 3.58 Bohr magnetons, assuming Russell-Saunders coupling and multiplet intervals which are large compared to kT .

The present data can be interpreted on the basis of a $5f^2$ configuration perturbed by a nonspherically symmetric electric field. Preliminary calculations with a field of cubic symmetry²³ and an overall splitting of the 3H_4 multiplet of 221 cm^{-1} provide a reasonable fit to the data. A comparison of the calculated and measured susceptibilities is given in Table 20. The agreement between the theoretical and experimental susceptibilities is considered to be reasonably good.

Table 20

COMPARISON OF CALCULATED AND MEASURED
SUSCEPTIBILITIES OF URANIUM IN UCd_{11}

Temperature (K)	$M\chi_U \times 10^3$	
	Calculated	Measured
4.2	38.9	39.0
63.2	21.8	17.2
77.2	18.5	15.1
296.2	5.34	5.28

²³Penney, W. G., and Schlapp, R., Phys. Rev., 41, 194 (1932).

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES*

The development of a Direct Fluorination Volatility Process for the recovery of uranium and plutonium from irradiated nuclear reactor fuels was continued. In this process, uranium and plutonium dioxides are fluorinated to produce hexafluoride products, which are then decontaminated by volatility techniques.

Separation of uranium hexafluoride from plutonium hexafluoride by thermal decomposition of the latter was investigated further. The studies indicated that practical rates of separation could be achieved between 200 and 300 C.

Studies of the decomposition of plutonium hexafluoride by gamma radiation were made to obtain information concerning the extent of decomposition, the products of decomposition, and the fundamental processes involved in the radiation chemistry of plutonium hexafluoride. The synthesis of uranium hexafluoride by the action of gamma radiation on mixtures of plutonium tetrafluoride and elemental fluorine was also studied.

Additional work was carried out on a fluidization-volatility scheme for the recovery of uranium from enriched uranium-zirconium alloy fuels. This process involves a chlorination of the alloy, while it is submerged in an inert fluidized bed, and a subsequent fluorination step. The zirconium is separated as the volatile tetrachloride during the chlorination step. The uranium is recovered as the volatile hexafluoride during the fluorination step.

Studies were continued on a fluid-bed-pyrohydrolysis reaction scheme for the disposal of waste zirconium tetrachloride produced during the chlorination of uranium-zirconium alloy fuels. In the reaction, the tetrachloride is converted into the more easily stored oxide. Preliminary studies were also made of an alternative scheme for processing the zirconium tetrachloride off-gas. In this scheme static beds of rock salt were used for the absorption of the tetrachloride.

Additional studies were made of the conversion of uranium hexafluoride to high-density uranium dioxide particles by the simultaneous reaction of the hexafluoride with steam and hydrogen.

*A summary of this section is given on pages 7 to 12.

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

1. Separation of Mixtures of Uranium and Plutonium Hexafluorides by Selective Thermal Decomposition of Plutonium Hexafluoride
(L. Trevorrow, J. Riha)

A mixture of uranium hexafluoride and plutonium hexafluoride will be produced by the fluorination of uranium dioxide nuclear fuel in the Direct Fluorination Volatility Process. Since plutonium hexafluoride is much less stable than uranium hexafluoride, thermal decomposition can be used to separate the components of the mixture. To effect the separation, a mixture of the hexafluorides is passed through a vessel heated to a temperature at which plutonium hexafluoride decomposes rapidly to plutonium tetrafluoride, but at which uranium hexafluoride is stable.

The results of previous work were reported in ANL-6543, page 115. Additional experiments have been carried out which have yielded information about both the efficiency and the rate of separation obtained by thermal decomposition.

The experiments were carried out in the apparatus that was previously described (see ANL-6543, page 116, Figure 33, Apparatus Used for Set 2). A different vessel was used for each thermal decomposition reported here. The vessels were 2 in. in diameter and 2 in. in length, and were packed with nickel wool to increase the interior surface area to about 1.5×10^3 sq cm. The temperature of the vessel was measured by a thermocouple in a well which extended down into the center of the vessel. Fluorine at one atm pressure was circulated through each vessel at 300 C, and then plutonium hexafluoride vapor was circulated through the vessel at 250 C to deposit 4 to 6 g of plutonium tetrafluoride in it. This deposit of plutonium tetrafluoride was formed prior to the separation experiments described below.

In a typical experiment, a mixture of uranium hexafluoride (~90 mm), plutonium hexafluoride (~10 mm), and helium (~660 mm) was circulated through the system at room temperature for 2 hr, during which time the decomposition vessel was bypassed. The mixture was then sampled. After the sampling, the mixture was circulated through the decomposition vessel at a flow rate of 800 ml/min for a given length of time, and a final sample of the gas was taken. Gas samples were condensed onto frozen, aqueous solutions of aluminum nitrate in nitric acid. The frozen mixtures were melted to hydrolyze the hexafluorides, and the resulting solutions were analyzed to obtain the uranium and plutonium contents of the gas sample. The uranium and plutonium contents of the deposited solids in the reaction vessel were measured by cutting the vessel

open after the gas circulation had been completed, immersing the vessels in 6 molar nitric acid-0.1 molar aluminum nitrate solution to dissolve the solids, and analyzing the resulting solution.

Table 21 shows the results of the analyses of the gas samples and of the solids deposited from the gas mixtures. The ratios* of uranium to plutonium in the gas samples are plotted in Figure 48 as a function of total circulation time. The results at 150 C were obtained by sampling a mixture after various heating times.

Table 21

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

Mixtures of UF₆ (~90 mm), PuF₆ (~10 mm), and He (~660 mm) were circulated through nickel vessels packed with nickel wool. The volume of each packed vessel was 100 ml. The total volume of the system was 9300 ml.

No.	Temp Decomp Vessel (C)	Total Internal Geometric Surface Area (sq cm x 10 ⁻³)	Wt PuF ₄ Initially in Vessel (g)	Circulation Time ^a (hr)	Analysis of Gas Sample			Percentage of Initial Pu Removed from Gas ^b	Analysis of Solids Deposited from Gas Mixture		
					Wt U (mg)	Wt Pu (mg)	Ratio (U/Pu)		Wt U (g)	Wt Pu (g)	Percent U in Solids ^c
73 ^d	150	1.6	3.891	0	34.9	3.3	10.6	6			
				1-1/4	45.1	3.96	11.4	35			
				5	37.6	2.22	16.9	35	-	-	-
				10	30.6	0.76	40.0	69			
195	200	1.5	4.225	0	763	62.1	12.3				
				1-1/3	438	10.7	40.9	70.0	0.00092	0.37	0.25
129 ^d	200	1.4	4.117	0	429	28.3	15.2				
				4	411	0.164	2.51 x 10 ³	99.4	0.0044	0.66	0.67
180	200	1.6	4.456	0	504	39.5	12.8				
				10	472	0.0243	1.94 x 10 ⁴	99.9	-	-	-
188	300	1.6	3.810	0	477	48.3	9.90				
				1-1/3	397	0.114	3.48 x 10 ³	99.7	0.00098	1.08	0.091
191	300	1.6	4.218	0	456	26.4	17.3				
				2-2/3	474	0.0772	6.17 x 10 ³	99.7	0.00172	0.655	0.26
137 ^d	300	1.6	4.644	0	445	37.4	11.9				
				4	406	0.147	2.76 x 10 ³	99.5	0.0030	0.84	0.36
178	300	1.5	5.370	0	511	38.6	13.2				
				10	472	0.13	3.63 x 10 ³	99.6	0.0081	0.60	1.3

^a One hour of circulation time is equivalent to a 0.65-min residence time of the entire sample in the decomposition vessel.

^b Percentage Pu removed from gas = $\frac{(\text{Pu/U})_{\text{initial}} - (\text{Pu/U})_{\text{final}}}{(\text{Pu/U})_{\text{initial}}} \times 100$.

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

^d Results of Experiments 73, 129, and 137 were reported previously in ANL-6543, page 118, but are repeated here to allow comparison with results of recent experiments.

The best separation was obtained at 200 C when a mixture with an initial ratio of uranium to plutonium of 12.8 was circulated through the vessel for 10 hr. (This was equivalent to a residence time in the decomposition vessel of 6.6 min for the entire mixture.) The ratio of uranium to plutonium increased to 1.94×10^4 , indicating a removal of

*The ratios of uranium to plutonium are of the same order of magnitude as those that will be of significance in the separation step of the Direct Fluorination Process.

99.9 percent of the initial plutonium from the gas. At 300 C, the maximum ratio of uranium to plutonium was reached much more rapidly. During a circulation time of $1\frac{1}{3}$ hr (residence time of 0.88 min) through a vessel at 300 C, the uranium-to-plutonium ratio of a gas mixture was increased from 9.88 to 3.48×10^3 , indicating a removal of 99.7 percent of the initial plutonium from the gas. The extent of the separation at equilibrium decreases as the temperature of the vessel increases. This relation is expected because the equilibrium constant $(\text{PuF}_6)/(\text{F}_2)$ for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{PuF}_6(\text{g})$ increases with temperature (see ANL-6101, page 80). The rate of separation increases with temperature since the rate of decomposition of plutonium hexafluoride vapor increases with temperature (see ANL-6333, page 133).

Figure 48

CHANGE OF URANIUM-TO-PLUTONIUM RATIO OF URANIUM
HEXAFLUORIDE-PLUTONIUM HEXAFLUORIDE MIXTURES
DURING CIRCULATION THROUGH HEATED VESSELS

Flow Rate: 800 ml/min
 Interior Surface Area of Vessels: $\sim 1.5 \times 10^3$ sq cm
 Volume of Vessel: 100 ml
 Volume of Total System: 9300 ml
 Residence Time: $0.011 \times$ Circulation Time

The percentage of uranium in the solids as shown in Table 21 increased with the total circulation time (or residence time of the total gas mixture in the hot vessel) for the set of experiments at 300 C. The purest plutonium tetrafluoride product was obtained in Experiment 188, in which a gas mixture with an initial concentration of 90.8 percent uranium hexafluoride in total hexafluorides was circulated through a vessel for $1\frac{1}{3}$ hr (residence time of total mixture, 0.88 min) at 300 C to deposit plutonium tetrafluoride with a uranium content of 0.091 percent.

It is concluded that thermal decomposition can be used to separate plutonium hexafluoride from uranium hexafluoride between 200 and 300 C at rates which are practical for application to the fluoride volatility processing of power reactor fuels.

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

Glove-box enclosures which are used for the handling of plutonium hexafluoride have filters attached to the inlet and outlet of the ventilation system of the enclosures to prevent the discharge of particulate matter containing plutonium. Since plutonium hexafluoride will react very rapidly with water vapor in the glove-box atmosphere, an investigation was made of the factors which will affect the filtration of plutonium-bearing particulate matter obtained through the hydrolysis of plutonium hexafluoride. The filters evaluated were AEC type filters used in glove-box installations at Argonne National Laboratory.

Particle penetration data were obtained from experiments in which small-scale controlled releases of plutonium hexafluoride, 25 mg or less, were made into an atmosphere of known moisture content. The resulting air mixtures were passed through AEC filters, a water bubbler, and Millipore filters in series, at a controlled flow rate. Gamma and/or alpha counts of the filters and bubbler were used to determine penetration for individual filters and combinations of filters.

The apparatus consisted of a 385-ml glass mixing chamber attached to a heated enclosure which contained the nickel release vessel containing the plutonium hexafluoride. The plutonium hexafluoride was discharged into the mixing chamber. Prior to admitting air to the mixing chamber, the moisture content of the air was controlled by mixing dry air with humidified air. The humidity of the mixed air was measured by means of an automatic dew-point recorder. (A more detailed description of the equipment and the experimental procedure have been reported previously in ANL-6477, page 114.)

The experimental results are presented in Table 22. Corrected values for experimental results reported previously (see ANL-6477, page 117, and ANL-6543, page 127) are included in Table 22. The penetration values were revised based on the correction of the count contribution of the AEC filter backing screen.

In Figure 49 the log of the ratio of plutonium passing through two AEC filters to the plutonium released is plotted against the log of the ratio of moles of plutonium hexafluoride to moles of water initially present in the mixing chamber. The amount of plutonium hexafluoride released varied between 1.5 and 25 mg. The moisture content of the air

varied between 0.9 and 11 mg of water per liter of air. The air velocity through the filters was 1.0 cm/sec in all experiments. When there was sufficient moisture in the air to hydrolyze completely the plutonium hexafluoride released, the penetration of two AEC filters in series varied from one ppm to 2 ppb. Some of the scatter of the data may be attributed to the variation of turbulent flow in the mixing chamber, variation in different samples of filter media, and variation in particle agglomeration. The curve in Figure 49 is drawn through points of maximum penetration.

Table 22

FILTRATION RESULTS FROM PLUTONIUM HEXAFLUORIDE RELEASE

Air Velocity at Filters: 0.97 cm/sec Mixing Chamber Volume: 385 ml Air Flow Rate: 0.5 liter/min Area of Each Filter: 8.6 sq cm								
Exp. No. ^a	Partial Pressure of H ₂ O in Air Used (mm Hg)	Wt PuF ₆ ^b Released (mg)	($\frac{\text{PuF}_6}{\text{H}_2\text{O}}$) ^c Mole	γ cpm on 1st AEC Filter	γ cpm ^d Beyond 1st AEC Filter	% Penetration ^e 1st AEC Filter	γ cpm Beyond 2nd AEC Filter	% Penetration ^e 1st and 2nd AEC Filters
4	9.20	1.5	0.022	1.51×10^4	0.077	0.00051	0.061	0.00040
25	10.64	2.9	0.037	1.60×10^5	1.00	0.00063	0.072	0.00045
24	9.20	2.8	0.041	1.35×10^5	1.24	0.00092	0.24	0.00018
23	10.26	5.3	0.071	2.83×10^5	4.53	0.0016	0.098	0.00035
20	7.07	4.0	0.077	1.48×10^5	0.46	0.00031	0.020	0.00014
26	9.88	8.3	0.115	4.57×10^5	0.31	0.000068	0.0011	0.0000024
27	9.88	12.4	0.172	6.19×10^5	0.27	0.000044	0.0096	0.0000016
30	9.20	12.4	0.184	7.12×10^5	0.32	0.000045	0.21	0.000029
2	7.62	10.4	0.186	1.39×10^5	0.21	0.00015	0.086	0.000062
22	10.64	14.5	0.186	7.75×10^5	11.9	0.0015	0.0018	0.0000023
31	9.88	15.3	0.212	6.94×10^5	0.13	0.000019	0.022	0.0000032
32	9.88	15.9	0.220	9.79×10^5	0.38	0.000039	0.26	0.000027
29	9.88	18.7	0.258	9.64×10^5	0.29	0.000030	0.22	0.000023
13	1.44	2.9	0.275	1.73×10^4	2.52	0.015	0.44	0.0025
33	9.88	20.4	0.282	9.42×10^5	0.26	0.000028	0.071	0.0000075
28	9.88	22.3	0.308	1.01×10^6	0.57	0.000056	0.50	0.000050
11	1.72	4.2	0.334	3.24×10^4	0.16	0.00049	0.051	0.00016
18	3.16	9.7	0.42	3.69×10^5	0.61	0.00017	0.51	0.00014
19	3.30	14.7	0.61	6.18×10^5	1.78×10^4	2.76	0.25	0.000040
14	1.37	9.5	0.95	1.85×10^5	304	0.16	0.23	0.00012
7	1.50	13.9	1.27	4.15×10^5	2.21×10^5	34.7	2323	0.56
9	1.25	12.0	1.31	3.66×10^5	2.71×10^4	6.90	47.1	0.013
10	1.37	14.7	1.47	4.12×10^5	4.42×10^4	9.70	0.30	0.000073
12	0.94	20.9	3.04	4.70×10^5	4.56×10^5	49.2	9.75×10^4	17.2
8	1.09	24.9	3.11	5.56×10^5	7.87×10^5	58.6	3.67×10^5	39.8
6	0.77	18.7	3.32	4.64×10^5	6.39×10^5	57.9	1.75×10^5	27.4

^a Experiment 2 and Experiments 4-13 were previously reported in ANL-6477, page 117, and ANL-6543, page 127.

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

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

^d Gamma count of less than 500 cpm computed from alpha count based on an alpha to gamma count ratio of 450.

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

The extrapolation of information obtained in these experiments to the filter systems of glove-box facilities used at Argonne for the handling of plutonium hexafluoride indicates that the installations can safely handle up to 50 g of plutonium hexafluoride when the partial pressure of water in the air is greater than 6.8 mm Hg. A partial pressure of 6.8 mm Hg is equivalent to a relative humidity of 40 percent at 67 F. Since the atmospheric content of water may decrease to as low as 0.3 mm Hg, humidification of the glove-box atmosphere may be necessary at times.

Figure 49

FRACTION OF RELEASED PLUTONIUM HEXAFLUORIDE PASSING THROUGH TWO AEC FILTERS

The size of particles produced by the vapor-phase hydrolysis of plutonium hexafluoride are being determined by examination with an electron microscope. Samples of the material have been collected by an electrostatic precipitator and by AEC filter media. Most of the hydrolyzed plutonium hexafluoride was found in the form of agglomerates. The agglomerates observed were found to have a wide size range and were composed of spherical particles from 0.01 to 0.2 μ in diameter. More work on this phase of the problem will be carried out.

3. Decomposition of Plutonium Hexafluoride by Gamma Radiation
(M. J. Steindler, D. V. Steidl)

The volatility of plutonium hexafluoride is utilized in the Direct Fluorination 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 plutonium hexafluoride 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 plutonium hexafluoride. The effect of inert gases on the decomposition is also being investigated.

The previous report on the decomposition of plutonium hexafluoride (see ANL-6477, page 118) summarized the available literature data on the decomposition of plutonium hexafluoride by alpha radiation and described the experimental procedures used in the present work. Briefly, the experimental procedure was the following. Samples of purified plutonium hexafluoride were introduced into nickel vessels and irradiated in the Argonne High-level Gamma-irradiation Facility. After irradiation, the contents of the vessels were analyzed to determine the residual plutonium hexafluoride and the quantity of fluorine and plutonium tetrafluoride formed. Data obtained in initial experiments, summarized previously in ANL-6477, page 121, Table 33, showed an increase of the extent of decomposition with increasing amounts of energy absorbed by the plutonium hexafluoride. Plutonium tetrafluoride and fluorine were identified as the products of the decomposition.

In recent experiments, the range of energy absorbed by plutonium hexafluoride has been extended. Data on the gamma decomposition of plutonium hexafluoride in the absence of inert gases are summarized in Table 23. These data, corrected for the decomposition of plutonium hexafluoride by alpha radiation to the extent of 0.22 percent per day, show the relation between the amount of plutonium tetrafluoride formed and the amount of energy absorbed by plutonium hexafluoride. This relation is linear within the range of the energy absorption studied. The data of Table 23 together with those presented previously (see ANL-6477, page 121) yield a slope of approximately 7.2 molecules per 100 ev absorbed in plutonium hexafluoride. These data are plotted in Figure 50. The single experiment, Experiment 26, carried to very high energy absorption gave an anomalous value which cannot be explained at this time. Additional experiments at high absorbed energies are planned. The magnitude of the G value (number of molecules decomposed or formed per 100 ev) precludes a chain reaction mechanism for the decomposition, but no distinction can be made between ionic and excitation processes in the decomposition. It is likely that both types of processes contribute to the decomposition.

Table 23

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION

Average Gamma Energy:		0.75 Mev					
Dose Rate:		1×10^4 to 4×10^4 rad/min					
Temperature:		60-70 C					
Plutonium Hexafluoride Pressure:		Approximately 100 mm Hg at 25 C					
Exp.	Initial PuF_6 (millimoles)	Fricke Dose ^a (rad $\times 10^{-8}$)	Absorbed Dose ^b (ev $\times 10^{-20}$)	PuF_4 Formed ^c (millimole)	PuF_6 Lost ^d (millimole)	GPuF_4 ^e	GPuF_6 ^f
183-4	1.057	1.07	18.8	0.285	0.275	9.1	8.8
157-1	1.113	1.48	23.9	0.282	0.270	7.7	6.8
173-1	1.031	2.01	28.7	0.405	0.317	8.5	6.6
191-1	2.076 ^g	0.98	31.2	0.372	0.333	7.2	6.4
26	1.025	2.95	42.3	0.248	0.302	3.5	4.3

^aBased on aqueous dosimetry.

^bCalculated from the Fricke Dose and the ratio of electron densities of water and gaseous PuF_6 .

^cBy chemical analysis of the solid residue.

^dFrom PVT data.

^eBased on PuF_4 formed.

^fBased on PuF_6 decomposed.

^gInitial PuF_6 pressure: 167.9 mm Hg at 25 C.

In the experiments reported in Table 23, it is assumed that the absorption of energy in gaseous plutonium hexafluoride is directly proportional to the electron density of the medium and can thus be calculated from the Fricke dose obtained in an aqueous medium. While

Fricke dosimetry is carried out in polystyrene vials and not in nickel, the minor attenuation of the gamma radiation by the nickel walls of the irradiation vessels used with plutonium hexafluoride has been ignored. The direct absorption of gamma radiation by gaseous plutonium hexafluoride is considered to be of minor importance compared with the total energy absorbed. The absorbed energy as determined from the Fricke dose and the ratio of electron densities of liquid water and gaseous plutonium hexafluoride is therefore believed to be sufficiently precise for use in this study. On the basis of these energy data, the calculated values of the G factor are believed to reflect adequately the decomposition of plutonium hexafluoride per 100 ev absorbed by plutonium hexafluoride.

Figure 50
DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY GAMMA
RADIATION

In order to determine the effects of inert gases on the decomposition of plutonium hexafluoride, several experiments were carried out on the radiation decomposition of mixtures of plutonium hexafluoride and inert gases. The results of these experiments are summarized in Table 24.

Table 24

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION IN THE PRESENCE OF INERT GASES

		Average Gamma Energy:		0.75 Mev				
		Dose Rate:		1×10^4 to 4×10^4 rad/min				
		Temperature:		60-70 C				
		Plutonium Hexafluoride Pressure:		Approximately 90 mm Hg at 25 C				
		Inert Gas Pressure:		Approximately 700 mm Hg at 25 C				
Exp.	Initial PuF ₆ (millimoles)	Inert Gas (millimoles)	Fricke Dose ^a (rad x 10 ⁻⁸)	Absorbed Dose ^b (ev x 10 ⁻²⁰)	PuF ₄ Formed ^c (millimole)	PuF ₆ Lost ^d (millimole)	G _{PuF₄} ^f	G _{PuF₆} ^f
7-3	1.073	8.132 He	1.00	15.6	0.222	0.252	8.6	9.7
24	1.093	8.134 He	1.96	26.3	0.403	0.558	8.1	12.8
34	1.035	17.16 He ^e	0.98	15.6	0.203	0.150	7.8	5.8
10	1.097	17.29 He ^e	1.01	16.8	0.183	0.184	6.6	6.6
15	1.074	8.146 Kr	0.99	15.1	0.332	0.313	13.2	12.5
30	1.006	9.238 Kr	1.00	13.8	0.352	0.346	15.4	15.1
36	1.020	7.958 O ₂	0.99	16.1	0.039	0.075	1.5	2.8
20	1.088	8.676 O ₂	1.00	16.7	0.063	0.154	2.3	5.6

^a Based on aqueous dosimetry.

^b Calculated on the basis of the Fricke dose and the ratio of electron densities of water and gaseous plutonium hexafluoride. The dose calculated in this manner represents the energy absorbed in PuF₆ only and does not reflect the energy absorbed in the inert gas.

^c By chemical analysis.

^d From PVT data.

^e Helium pressure: approximately 1300 mm Hg.

^f Calculated from the absorbed dose. See footnote "b."

A comparison of the G values obtained in experiments using helium with those obtained in experiments carried out in the absence of helium indicates that helium is without appreciable effect on the decomposition. This may be attributed to the small contribution of helium to the total electron density of the mixtures, coupled with the high ionization potential (24.58 ev) and the high energy of the first electronic excited state of helium (~20 ev), resulting in an improbable energy transfer between plutonium hexafluoride and helium.

On the other hand, krypton appears to enhance slightly the gamma decomposition of plutonium hexafluoride. The results shown in Table 24 have been calculated on the basis of energy absorption in plutonium hexafluoride only. The contribution made by krypton to the total electron density of the gaseous mixture is relatively large and thus krypton absorbs appreciable amounts of energy when compared with plutonium hexafluoride.

An efficiency factor e may be defined as

$$e = \frac{\text{molecules of PuF}_6 \text{ decomposed by energy absorbed in Kr} / 100 \text{ ev absorbed in Kr}}{\text{molecules of PuF}_6 \text{ decomposed by energy absorbed in PuF}_6 / 100 \text{ ev absorbed in PuF}_6},$$

from which it is possible to estimate the efficiency of krypton relative to plutonium hexafluoride toward the decomposition of plutonium hexafluoride. The efficiency factor may be rewritten in the form

$$e = \frac{G_{\text{PuF}_4}^{\text{Kr}} - G_{\text{PuF}_4}}{G_{\text{PuF}_4}} \frac{E^{\text{PuF}_6}}{E^{\text{Kr}}},$$

where $G_{\text{PuF}_4}^{\text{Kr}}$ is the G value for the formation of plutonium tetrafluoride calculated from experiments using krypton and based on the energy absorption in plutonium hexafluoride only; G_{PuF_4} is the G value obtained from experiments on the decomposition without krypton; E^{PuF_6} is the energy absorbed by plutonium hexafluoride in the experiment using krypton; and E^{Kr} is the energy absorbed by krypton in the same experiment. It is assumed that the G value for the decomposition of plutonium hexafluoride due to energy absorbed in plutonium hexafluoride is the same in experiments using krypton as an additive as it is in experiments without krypton. Table 25 illustrates the magnitude of the efficiency factor for experiments using krypton as the inert gas. On the basis of these data, the efficiency of krypton in decomposing plutonium hexafluoride is approximately 30 percent that of plutonium hexafluoride. Although charge transfer between unexcited krypton ions and plutonium hexafluoride is not energetically possible, the transfer of energy from excited states of krypton to plutonium hexafluoride with subsequent decomposition of plutonium hexafluoride is a possible mechanism for the decomposition. The observation

that plutonium hexafluoride decomposes photochemically²⁴ indicates that the decomposition of plutonium hexafluoride by transfer of excitation energy is possible. The contribution of ionization processes to the radiation decomposition mechanism is not yet clear.

Table 25

EFFICIENCY FACTORS FOR INERT GASES IN THE GAMMA-RADIATION
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE

Exp.	$G_{\text{PuF}_4}^{\text{M}}$ ^a	$G_{\text{PuF}_4}^{\text{b}}$	E^{PuF_6} ^c (ev x 10 ⁻²⁰)	E^{M} ^d (ev x 10 ⁻²⁰)	$E^{\text{PuF}_6}/E^{\text{M}}$	$G_{\text{PuF}_4}^{\text{M}} - G_{\text{PuF}_4}$	e ^e
15-Kr	13.2	7.2	15.1	32.9	0.459	5.0	0.32
30-Kr	15.4	7.2	13.8	37.5	0.368	8.2	0.42
20-O ₂	2.3	7.2	16.7	15.7	1.06	-4.9	-0.72
36-O ₂	1.5	7.2	16.1	14.2	1.13	-5.7	-0.89

^a $G_{\text{PuF}_4}^{\text{M}}$ is the G value computed from the amount of PuF₄ formed in an experiment using the additive gas M, based on the energy absorbed in PuF₆ only.

^b G_{PuF_4} is the G value computed from the amount of PuF₄ formed in an experiment without additive gas, based on the energy absorbed in PuF₆. The value of 7.2 represents the average G for experiments summarized in Table 23 and in ANL-6477, Table 33.

^c E^{PuF_6} is the energy absorbed by PuF₆ in the experiment using an additive gas.

^d E^{M} is the energy absorbed by the additive gas M.

^e The efficiency factor e is given by the relation

$$e = \frac{G_{\text{PuF}_4}^{\text{M}} - G_{\text{PuF}_4}}{G_{\text{PuF}_4}} \frac{E^{\text{PuF}_6}}{E^{\text{M}}}$$

As is evident from the data in Table 24, oxygen appears to depress the decomposition of plutonium hexafluoride by gamma radiation. This is reflected in the calculated efficiency factors for the oxygen experiments, illustrated in Table 25. The data in Table 24 have not been corrected for the loss of plutonium hexafluoride by reaction with oxygen in the absence of gamma radiation. Preliminary results indicate that the correction may be appreciable and may result in an even lesser decomposition by gamma radiation than indicated in Tables 24 and 25. While the exact role of oxygen in this system has not been defined, the well-known ability of molecular oxygen to act as a radical scavenger in photochemical and radiochemical reactions leads to the tentative conclusion that deactivation of plutonium hexafluoride may represent one of the mechanisms responsible for the decrease in the extent of decomposition.

²⁴Weinstock, B., and Malm, J., J. Inorg. Nucl. Chem., 2, 380 (1956).

4. Formation of Plutonium Hexafluoride by Gamma Irradiation of Mixtures of Plutonium Tetrafluoride and Fluorine
(M. J. Steindler, D. V. Steidl)

As part of the study of the radiation chemistry of plutonium fluorides, the reaction of fluorine and plutonium tetrafluoride has been investigated in the presence of gamma radiation. This reaction is the reverse of the radiation-induced decomposition reaction. The synthesis of plutonium hexafluoride by gamma irradiation of mixtures of fluorine and plutonium tetrafluoride may be compared with the same process carried out by thermal activation.

Samples of finely divided plutonium tetrafluoride and elemental fluorine were placed in cylindrical nickel vessels or in $\frac{3}{4}$ -in.-OD nickel test tubes fitted with nickel valves. The plutonium tetrafluoride was obtained by decomposition of plutonium hexafluoride at room temperature by alpha radiation. The mixtures of plutonium tetrafluoride and fluorine were irradiated in the Argonne High-level Gamma-irradiation Facility. After irradiation, the vessels were cooled to -80 C and the fluorine was evacuated from the mixture. The volatile products of the irradiation were removed from the solid plutonium tetrafluoride by vacuum distillation and were analyzed for plutonium content.

The volatile product obtained from irradiation of mixtures of plutonium tetrafluoride and elemental fluorine was identified as plutonium hexafluoride by its infrared spectrum.²⁵ The observed vapor pressure of the volatile product at the ice point (17 mm Hg) agreed with the known vapor pressure of plutonium hexafluoride at that temperature (17.9 mm Hg).²⁶

The presence of both a solid and a gas phase in this system complicates the estimation of the absorbed dose. Although it may be possible to obtain an estimate of the absorbed dose in the solid phase by utilizing assumptions similar to those described previously for the decomposition of gaseous plutonium hexafluoride, information about the mechanism of the formation of plutonium hexafluoride is required before the calculated absorbed dose becomes meaningful. In the absence of information as to the identity of the activated species or as to the nature of the formation process, such calculations have been omitted from Table 26, which summarizes the results.

The data indicate clearly that appreciable quantities of plutonium hexafluoride are formed by irradiation of mixtures of plutonium tetrafluoride and elemental fluorine. The observed pressures of plutonium

²⁵Malm, J., Weinstock, B., and Claasen, H., J. Chem. Phys., 23, 2192 (1955).

²⁶Weinstock, B., Weaver, E. E., and Malm, J., J. Inorg. Nucl. Chem., 11, 104 (1959).

hexafluoride are in most cases considerably greater than those which would be obtained if this system were allowed to reach equilibrium in the absence of gamma radiation.²⁷ It may be assumed that the success of the synthesis of plutonium hexafluoride, particularly at final pressures of the hexafluoride in excess of those that would be predicted from the thermodynamic equilibrium constant, is due in part to the slow thermal decomposition of the product at the temperatures of the irradiated vessel. Also, the decomposition of plutonium hexafluoride by gamma radiation is relatively unimportant at the low pressures of the hexafluoride.

Table 26

FORMATION OF PLUTONIUM HEXAFLUORIDE BY GAMMA IRRADIATION OF
PLUTONIUM TETRAFLUORIDE-FLUORINE MIXTURES

Average Gamma Energy: 0.75 Mev

Dose Rate: 1×10^4 rad/min to 4×10^4 rad/min
(Fricke Dosimeter)

Vessel Temperature: 60-70 C

Exp.	Initial PuF ₄ (millimoles)	Initial F ₂ ^a (mm Hg)	Fricke Dose ^b (rad $\times 10^{-8}$)	PuF ₆ Formed (millimole)	PuF ₆ Pressure ^c (mm Hg)
848F193	9.93	725	0.10	0.011 ^d	3.7 ^g
1026F123	2.03	731	1.09	0.019 ^e	19.7 ^h
1026F105	1.73	730	2.02	0.006 ^e	6.2 ^h
1026F133	2.04	745	3.08	0.006 ^e	6.2 ^h
1026F111-3	4.09	728	1.98	0.038 ^e	39.5 ^h
1026F75	9.79	738	1.00	0.131 ^d	44.5 ^g
1026F69	9.92	717	1.00	0.247 ^d	84.0 ^g
1026F145-7	6.39	730	2.10	0.007 ^e	7.3 ^h
1026F111-1	5.00	730	3.00	0.036 ^e	37.4 ^h
1026F145-1	9.48	730	2.02	0.015 ^e	15.6 ^h
1026F186	26.73	375	0.90	0.019 ^e	1.5 ⁱ
1026F95	23.27	716	1.08	0.046 ^d	15.6 ^g
1026F181	26.73	743	0.94	0.0005 ^e	0.04 ⁱ
1026F199	26.71	740	0.95	0.002 ^e	0.2 ⁱ
1026F194	26.71	188	1.00	0.002 ^e	0.2 ⁱ
1026F153	18.97	735	2.03	0.034 ^f	35 ^h
1199F13	26.71	204	2.01	0.005 ^f	0.4 ⁱ
1026F162	35.85	727	1.51	0.208 ^f	16.7 ⁱ
1026F175	26.75	727	2.06	0.014 ^e	1.1 ⁱ

^aInitial fluorine pressure at 25 C.

^bBased on aqueous dosimetry.

^cThe equilibrium pressure of plutonium hexafluoride in the presence of plutonium tetrafluoride and elemental fluorine at a pressure of one atmosphere and at 70 C is 0.053 mm Hg. Tabulated pressure data were calculated at 25 C.

^dBased on the weight loss of PuF₄.

^eFrom chemical analysis of the volatile reaction product.

^fFrom PVT data.

^g50-cc vessel.

^h18-cc vessel.

ⁱ230-cc vessel.

²⁷Trevorrow, L. E. et al., J. Phys. Chem., 65, 398 (1961).

The data shown in Table 26 indicate considerable scatter for experiments carried out under similar conditions. Although a correlation between the energy absorbed and the extent of decomposition has been obtained for the decomposition of plutonium hexafluoride by gamma radiation, calculation of the equilibrium condition in the system plutonium tetrafluoride-fluorine in the presence of radiation reveals no such dependence on the absorbed dose. The calculated equilibrium ratio of plutonium hexafluoride and plutonium tetrafluoride* based on estimates for the G values for the formation and decomposition reactions involves only the absorption of energy in the solid tetrafluoride and the gaseous hexafluoride. It is recognized that the energy absorbed in the solid phase may be dissipated without the formation of plutonium hexafluoride, particularly if the activated solid is inaccessible to fluorine. Further, since the measured yield of plutonium hexafluoride is the net yield, decomposition of plutonium hexafluoride by activated tetrafluoride during the diffusion of the hexafluoride out of the solid may be expected to strongly affect the results. In the light of these factors, the nonreproducibility of the results is within expectations.

5. Calculation of the Rate of Decomposition of Plutonium Hexafluoride by Alpha Radiation
(M. J. Steindler)

Little data are available which will permit the calculation of the rate of decomposition, due to alpha radiation, of plutonium hexafluoride both in the vapor phase as well as in the solid phase. It is possible, however, to estimate the rate of decomposition, if a suitable G value for the decomposition is available. The present calculation, using the G value (7 molecules/100 ev) obtained from the gamma-ray decomposition of plutonium hexafluoride,** results in values which are in reasonable agreement with the few available experimental results.

Calculation of the rate of alpha decomposition of plutonium hexafluoride requires certain assumptions which define the limitations of the calculation. Besides requiring the G value, the calculation requires knowledge of the rate of emission and energy of the alpha particles, and

*It is necessary to assume that elemental fluorine is present in sufficient quantity to fluorinate the tetrafluoride and that fluorine does not absorb appreciable amounts of energy. Using a G value of 0.05 for the formation of plutonium hexafluoride and a G value of 7 for its decomposition, the molar ratio of $\text{PuF}_6:\text{PuF}_4$ is calculated to be 6.3×10^{-3} at the temperature of the irradiation. This ratio is independent of the dose rate, the total exposure dose, and the volume of the system.

** Examples of the similarity in ionic yields for gamma radiation and alpha radiation in inorganic systems are given in Lea, D. E., Actions of Radiations on Living Cells, University Press, Cambridge, England (1955), p. 34ff.

the energy expended by alpha particles in plutonium hexafluoride. The specific alpha activity of plutonium hexafluoride is determined by its isotopic composition. Because of the unknown distribution of the solid decomposition product (PuF_4) of plutonium hexafluoride in the vessel containing plutonium hexafluoride, the contribution of the decomposition product to the total energy dissipated in the gas is not readily evaluated. It has therefore been assumed for the purpose of the calculation that the rate of alpha particle emission does not change with time, i.e., the decomposition product contributes alpha particles to the system in the same way as plutonium hexafluoride. The energy of the alpha particles can be obtained from the literature data on the decay of the isotopes of plutonium.

For the purpose of calculating the energy dissipated by an alpha particle passing through plutonium hexafluoride, it has been assumed that gaseous plutonium hexafluoride is contained in a spherical vessel of 3.175-cm radius.* The range of alpha particles in gaseous plutonium hexafluoride is a function of the pressure of plutonium hexafluoride and may be computed using the Bragg-Kleeman rule. The range may be expressed by the relation

$$R(\text{cm}) = \frac{67.6}{P(\text{cm})} ,$$

where R , expressed in centimeters, is the range of alpha particles having an initial energy of 5.15 Mev, and P is the pressure of gaseous plutonium hexafluoride, in centimeters of mercury. The energy dissipation per unit path length of alpha particles is related to the residual range by the Bragg curve. In the case of gaseous plutonium hexafluoride, the energy dissipated by an alpha particle originating within the spherical container and moving in a random direction may be computed by, for example, a Monte Carlo procedure. The problem of determining the average energy loss of alpha particles at four different plutonium hexafluoride pressures was programmed for the IBM 704 computer. The resulting numbers, expressed as $F(P,r)$, reflect the fraction of the initial energy lost by an average alpha particle starting at a random point within the sphere and moving in a random direction.

The number of molecules decomposed per unit energy dissipated in plutonium hexafluoride may be approximated by the G value for the decomposition. It is necessary to assume that the formation reaction, i.e., $\text{PuF}_4 + \text{F}_2 \rightarrow \text{PuF}_6$ does not take place and, although this assumption is not completely valid, the approximation is believed adequate for low fluorine pressures. In the case of decomposition in the solid, it is also

*A study of the decomposition of plutonium hexafluoride by alpha radiation in vessels of this size is currently under way at Argonne.

assumed that recombination does not take place. In every instance, the use of these assumptions leads to values for the decomposition rate which are greater than the true values.

The results of the calculations are expressed by the relation

$$\text{Rate of decomposition (\% per day)} = 0.458 GF(P,r) \quad ,$$

where G is the number of molecules of plutonium hexafluoride decomposed per 100 ev absorbed and $F(P,r)$, a function of pressure and the radius of the spherical vessel, represents the fraction of the initial alpha-particle energy expended in the plutonium hexafluoride. A summary of the data is given in Table 27. Although the calculated rate of decomposition at high pressures is greater than that observed, the data with plutonium hexafluoride at a pressure of 28 mm Hg are in reasonable agreement with the observations. The anticipated greater deviation between the calculated

Table 27

COMPARISON OF THE CALCULATED AND OBSERVED RATE OF
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY
ALPHA PARTICLES IN A SPHERICAL VESSEL

Energy of the Alpha Particles: 5.15 Mev
Radius of Spherical Container: 3.175 cm
 $G = 7$ molecules/100 ev

Pressure PuF ₆ (mm Hg)	Range ^a (cm)	F(P,r) ^b	Decomposition (% per day)	
			Calculated	Observed
28	24.21	0.0733	0.23	0.06-0.35 ^d
50	12.52	0.1335	0.43	-
100	6.76	0.2909	0.93	0.2 ^e
1000	0.67	0.9118	2.92	-
solid	0.002	1.000 ^c	3.21	0.6-2.4 ^{d,e,f}

^aRange of 5.15-Mev alpha particles in plutonium hexafluoride at the indicated pressure.

^bSee text.

^cAssumed.

^dWeinstock, B., et al., J. Inorg. Nucl. Chem., 2, 380 (1956).

^eSteindler, M., unpublished data.

^fFlorin, A. et al., J. Inorg. Nucl. Chem., 2, 368 (1956).

and observed rates of decomposition at higher pressures is evident in Table 27. Further, the observed data were not obtained in spherical vessels and represent decomposition rates averaged over long periods of time. It is clear, however, that the present data on the decomposition of plutonium hexafluoride obtained from experiments with gamma radiation are applicable to the calculation of the alpha decomposition of plutonium hexafluoride. Further, by computing the appropriate values for the function $F(P,r)$, the decomposition rate may be calculated for any pressure or any vessel geometry.

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

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

Development has continued of the Direct Fluorination Process applied to uranium dioxide fuel. In this process, the uranium and plutonium dioxides from discharged reactor fuel are reacted with fluorine directly to produce hexafluoride products, which are then decontaminated by volatility techniques. Engineering-scale studies thus far have been directed toward process optimization of the primary fluorination of uranium dioxide pellets. The major objectives of these studies have been to demonstrate short times (less than 20 hr) for batch fluorination and satisfactory efficiency (greater than 75 percent) of fluorine utilization under practical operating conditions. The reaction is carried out in a fluidized bed in which pellets (or pellet fragments) of uranium dioxide form a packed bed with fluidization provided by means of inert solid (alumina grain) in the space above and in the voids of the pellet bed. The fluidization aids in the heat transfer and in the mixing of solid fines formed as intermediates or residues in the system.

Early results (see ANL-6379, page 161) showed that reaction control could be obtained when fluidization of the alumina is maintained. The total surface area of uranium solids reacting to form hexafluoride was found to be governed largely by the amount of intermediate uranium compounds present in the system. The intermediates UO_2F_2 and U_3O_8 , which are highly reactive, appear mostly as fine particles (of $\sim 20\text{-}\mu$ diameter) of high specific surface area. Accordingly, for pellet beds in which low fluorine efficiencies are obtained, the introduction of oxygen has been shown capable of increasing both the reactivity of the system and the fluorine utilization. A 4.4-kg batch of pellets (of 6-in. initial depth) has been completely fluorinated in a satisfactory manner in about 6 hr at 500 C using a gas-recycle system to furnish oxygen and to minimize fluorine loss. This production rate is equivalent to about 50 lb UF_6 /(hr)(sq ft of reactor cross section).

In pellet beds of 18-in. depth investigated previously, caking tendencies, which resulted in poor temperature uniformity and/or poor gas contacting, were found for production rates above about $20 \text{ lb UF}_6/(\text{hr})(\text{sq ft of reactor cross section})$. Poor contacting was reflected in lower efficiency of fluorine utilization. However, these tests showed the benefit of close control of oxygen in improving fluidization behavior.

In the present period, several runs with 4.4-kg batches of uranium dioxide pellets (6-in.-deep beds) were carried out with continuous pellet additions to maintain a constant weight of pellets. After the reaction had proceeded for a period of time, the length of which depended upon the conditions of a run, it was presumed that a steady state is approximated wherein the pellet size distribution remains constant. As a consequence, other bed properties, such as bed depth and surface area, would also remain approximately constant. In one set of runs, the total gas rate (the rate of addition of fluorine and nitrogen) was varied, but no oxygen was added to the system. In another set of runs, the inlet oxygen concentration was varied while the total gas rate (the rate of addition of oxygen, fluorine, and nitrogen) was kept constant. The size distribution of pellet residues from the runs was examined.

Also, two batch runs were carried out with 12-in. (initial) beds using a two-zone reaction scheme. In the lower (uranium dioxide pellet) zone, the fluidization gas was an oxygen-nitrogen mixture. Fluorine was introduced above this pellet zone so that fluorination occurred in the upper zone in which fluidization was unhindered by the presence of the fixed pellet bed. Alumina grain was the fluidized medium in both zones of the reactor.

Initial Three Steady-state Runs

The initial set of runs, in which a constant weight of uranium dioxide pellets was maintained, were made at three different fluidizing gas rates in the range from 0.5 to 1.3 ft/sec. The fluorinations were carried out at 500 C with a 4.4-kg batch of uranium dioxide pellets and a once-through (no recycle) passage of gas containing 10 percent fluorine at the inlet. No oxygen was introduced in these runs, and an Alundum bed height of 12 in. (based on the empty column) was used. This amount of Alundum provided an Al_2O_3 -to- UO_2 weight ratio of 0.6. Whole pellets were added through an air-lock charger at about 1-hr intervals to maintain a constant weight of uranium dioxide pellets in the reactor.

Under these operating conditions (see Table 28, Runs UOF-56, -57, and -58), the production of uranium hexafluoride varied from 5.3 to 7.7 $\text{lb}/(\text{hr})(\text{sq ft reactor cross section})$ for the range of total gas rate from 0.5 to 1.35 ft/sec. The rate of production of uranium hexafluoride increased about 40 percent for a gas rate increase of 170 percent. These

data imply that the fluorination rate increases with the gas rate to about the $1/3$ power under the conditions of these experiments. Because of this small effect of gas rate, the fluorine utilizations were correspondingly lower at the higher gas rates. The chief significance of these runs was the low dependency on gas rate and the relatively low fluorine efficiency with a 6-in. bed (without recycle and with no added oxygen).

Table 28

RESULTS OF URANIUM HEXAFLUORIDE PRODUCTION RUNS UNDER APPROXIMATELY STEADY-STATE CONDITIONS

(Uranium dioxide pellets added during run)

Once-through Gas Flow

Weight of Pellets: 4.4 kg

Pellet Bed Height: 6 in.

Al₂O₃ Charge: 2.6 kg

Temperature: 500 C

Run No. (UOF-)	Duration (hr)	Alundum Bed Height ^a (in.)	Fluidization Velocity ^b (ft/sec)	Fluidizing Gas Composition				Bed Composition Ratio g Al ₂ O ₃ / g UO ₂	Fluorine Efficiency ^c (%)	UF ₆ Production Rate [lb/(hr)(sq ft)]
				F ₂ (vol %)	O ₂ (vol %)	N ₂ (vol %)	F ₂ /O ₂			
56	4	12	0.5	10	0	90	-	0.6	24.5	5.3
57	4.5	12	1.0	10	0	90	-	0.6	17.4	6.4
58	4	12	1.35	10	0	90	-	0.6	17.5	7.7
59	5	24	1.0	20	5	75	4	1.2	53.5	37.2
60 ^d	2	24	1.1	15	13	72	1.1	1.2	75.6	40.2

^a Based on empty column.

^b At operating conditions.

^c Fluorine efficiency based on rate of production of uranium hexafluoride.

^d Approximate steady-state conditions were achieved.

Runs Showing the Effect of Oxygen Concentration

Two experiments were made, Runs UOF-59 and UOF-60, in which the oxygen concentration was varied. These runs were carried out at 500 C, with a 6-in. pellet bed, a 24-in. Alundum bed, a superficial gas velocity of 1.0 ft/sec, and a fluorine concentration of 15 to 20 percent in the inlet gas. No gas recycle was used. In these runs a constant pellet bed weight was maintained by addition of pellets to the bed during the runs.

In UOF-59, the inlet gas contained 5.0 percent oxygen. Good temperature control was maintained in this run throughout the steady-state operating period of 5 hr. The total fluorine input and uranium hexafluoride collection are shown in Figure 51. Other data are summarized in Table 28. A constant fluorine concentration of 20 percent was maintained in the inlet gas.

In Run UOF-60, the inlet gas contained 13 percent oxygen. Within a period of 2 hr, a poor heat transfer condition developed, as shown by increased temperature differences among thermowells at various positions in the bed and the inability to maintain the prescribed rate of fluorine addition without exceeding the set temperature point at the control point.

(When the set temperature at the control is exceeded, the fluorine rate is automatically reduced.) As a result, the initial fluorine inlet concentration of 20 percent was reduced, and an average fluorine inlet concentration of 15 percent was realized during the run period. This condition of poor quality of fluidization was considered to be a result of accumulation of fines, and the run was terminated in order to examine the bed. Measurements made during the run are reported in Table 28.

Figure 51

STEADY-STATE FLUORINE EFFICIENCY AS DETERMINED
BY FLUORINE INTRODUCTION AND URANIUM
HEXAFLUORIDE COLLECTION

(Run UOF-59)

The rates of uranium hexafluoride production, 40 lb/(hr)(sq ft), were nearly the same in Runs UOF-59 and UOF-60. Fluorine utilization efficiency was higher (76 percent) at the higher oxygen concentration (13 percent) than the fluorine efficiency (56 percent) at the lower oxygen concentration (5 percent). Although these production rates and fluorine efficiencies are considered to be promising for a practical process, only the lower oxygen concentration is acceptable on the basis of fluidization quality. It is considered that these runs show the range of allowable fluorine-to-oxygen ratios in the pellet bed: a ratio of 4 to 1 is satisfactory (UOF-59), whereas a ratio of 1 to 1 appears to be too low (UOF-60).

At the end of UOF-60, the bed was examined, and a small portion, consisting mostly of Alundum through which some blackish (uranium oxide) fines were interspersed, was found to be agglomerated. The agglomerated material formed a very soft, porous cake, which was similar to that formed in a previous run with high oxygen concentration (UOF-53).

The pellet fragments remaining from the steady-state runs (UOF-56 through -60) were examined. As expected, a wide range of pellet sizes was observed. Some pellets that were added toward the end of the runs appeared to be nearly intact, while fragments and small pellet remains of about $\frac{1}{8}$ in. were also present. A photograph of pellet fragments from Run UOF-60 is shown in Figure 52. Such a range of sizes is believed to be even wider than that obtained from the type of pellet cracking expected from reactor fuel pellets irradiated to high burnups. Thus, the steady-state runs may simulate the state of fragmentation of highly irradiated pellets more closely than runs in which whole pellets were charged.

Figure 52
PELLET FRAGMENTS REMAINING
AT TERMINATION OF STEADY-
STATE RUN
(Run UOF-60)

Discussion of Caking Tendencies

The presence of relatively high concentrations of fines of intermediate compounds of uranium, such as U_3O_8 , has been correlated positively with both high fluorine efficiencies and caking tendencies in pellet beds. Fines (particles with dimensions less than 50μ) are known to exhibit poor fluidization quality, with resultant poor solids mixing and poor solid-gas contacting. Passage of gas through such fine powders results in severe gas channelling and/or bed slugging rather than in desirably smooth fluidization. However, by themselves, such powders do not "set up" in cakes unless some reaction occurs in which a solid product is formed or a high-temperature sintering action takes place. This freedom from caking has been shown in "mockup" fluidization tests of U_3O_8 powder. However, in the Direct Fluorination Process, since opportunity

exists for complex exothermic oxidation and fluorination reactions, caking can take place. Consequently, initially poor-quality fluidization may produce incipient caking conditions, and continuing reaction may lead to progressively more serious cake formation.

The maximum caking tendency would occur in the upper part of a pellet bed. Oxygen, uranium hexafluoride, and fines are produced in the lower part of the bed. The fines are carried upward (by elutriation) in gas depleted of fluorine (which could convert fines to volatile products). Consequently, the tendency for conditions unfavorable to fluidization to develop appears to be greatest at the top of the bed.

On the basis of the foregoing discussion, the following conditions appear to be desirable for the prevention of cake formation:

1. high-quality fluidization, i.e., good solids mixing and good solids-gas contacting;
2. low concentration of fines; and
3. elimination or minimization of gases capable of reactions with fines to form other solid products (e.g., elimination of uranium hexafluoride from zones in which it may react with uranium oxides or oxyfluorides).

Various methods of reducing caking tendencies are suggested by these conditions. One approach is the reduction of the amount of material in the uranium dioxide pellet bed, which is both a chemical source of fines and a physical hindrance to high-quality fluidization. Another approach is the reduction of the amount of fines by minimization of oxygen. Conditions favoring formation of solids may also be avoided by minimizing uranium hexafluoride concentration and by assuring the presence of an excess of fluorine throughout the reactor. The main practical problems in applying these schemes directly are associated with small pellet beds and high fluorine excesses. In the former case, batch operation is too short to be economical and provision for continuous pellet addition is required. In the latter case, recovery of unreacted fluorine in the effluent gas stream is required to avoid high fluorine costs.

In the present investigations, a two-zone reaction scheme is being used in an attempt to reduce caking tendencies. In this scheme, the lower zone is formed by the uranium dioxide pellet bed and the upper zone is formed by a region of fluidized Alundum grain. The Alundum also fills the voids of the pellet bed. A mixture of oxygen and nitrogen, which serves as the fluidizing gas, is introduced into the bottom of the pellet zone. Fluorine is introduced at the bottom of the upper zone, just above the pellet bed. Uranium oxide fines are formed in the lower zone and are elutriated

into the upper zone, where they are removed by fluorination. A schematic diagram of the fluorinator is shown in Figure 53.

One advantage of this two-zone scheme is the possibility that caking due to reactions of uranium hexafluoride with uranium oxides may be minimized. Another anticipated advantage is that the quality of fluidization in the upper zone will be improved by the absence of uranium dioxide pellets. Also, heat removal in the two-zone scheme is more favorable than in the one-zone scheme. This arises from the fact that only the oxidation reaction (with $\Delta H = -26$ kcal/g-mole uranium at 25 C) takes place in the pellet bed and fluorination of the fines (with $\Delta H = -231$ kcal/g-mole uranium at 25 C) takes place in the upper unhindered fluidized bed of Alundum. This more favorable heat condition should minimize the possibility of sintering and should reduce caking.

Initial Two-zone Reactor Operation

Two exploratory runs employing the two-zone scheme for the oxidation-fluorination of uranium dioxide pellets have been made. The first two-zone experiment (UOF-61) utilized an 8.8-kg batch of uranium dioxide (12-in. deep bed of $\frac{1}{2}$ -in. $\times$ $\frac{1}{2}$ -in. pellets) and sufficient Alundum (6.8 kg) to provide 24 in. of static bed above the pellets. The run was carried out batchwise at 500 C, and the oxygen and fluorine concentrations were varied during the run to observe the effects of these variables. The uranium hexafluoride production rates are shown in Figure 54, and the operating conditions and results are summarized in Table 29.

As seen in Figure 54, the uranium hexafluoride production rate appeared to vary considerably with increasing rates of oxygen introduction. Higher rates were obtained for higher oxygen concentrations in the range of about 3 to 7 percent. In the period of highest rate of oxygen introduction, mechanical vibration of the column also was used, and this appeared to have a large effect on the production rate, which rose to a maximum of about 90 lb UF_6 /(hr)(sq ft).

The fluorine utilization efficiency increased with production rate, as expected for constant fluorine introduction. Calculated oxygen reaction efficiencies during the run varied from 8 to 20 percent.

Figure 54

URANIUM HEXAFLUORIDE PRODUCTION
RATES. TWO-ZONE OXIDATION-
FLUORINATION OF URANIUM
DIOXIDE PELLETS
(UOF-61)

3-in. Finned Reactor
12-in. Pellet Bed
24-in. Al_2O_3 Bed Above Pellets (static)
Temperature: 500 C
Once-through Gas Flow

Table 29

OPERATING CONDITIONS AND RESULTS OF TWO-ZONE OXIDATION-FLUORINATION OF URANIUM DIOXIDE PELLETS

(Run UOF-61)

3-in. Finned Reactor
Temperature: 500 C
 UO_2 Charge: 8.8 kg (12-in. bed of 1/2-in. pellets)
 Al_2O_3 Charge: 6.8 kg

Run Time (hr)	Gas Flow in Pellet Bed			Gas Flow in Alumund Bed			Fluorine Efficiency		Avg Rate of UF_6 Production for Period [lb/(hr)(sq ft)]	Comment
	u_f^a (ft/sec)	O_2 (%)	Oxygen Efficiency ^c (%)	u_f^a (ft/sec)	O_2 (%)	F_2 (%)	Cumulative ^d (%)	For Period ^d (%)		
0 - 4.0	1.1	3.3	8	1.2	3.1	5.1	31	35	11	No vibration
4.0- 9.0	1.1 ^b	6.2	9	1.4	5.5	11.5	37	38	25	No vibration
9.0-10.3	1.2	7.6	8	1.4	6.6	13.1	37	37	27	No vibration
10.3-13.5	1.2	7.6	20	1.4	6.6	13.1	61	98	70	With vibration

^a Superficial fluidization velocity based on empty column at operating conditions.

^b Temperature: 425 C.

^c Estimate based on assumption that oxygen reacts to form uranium hexafluoride product according to the reactions $\text{UO}_2 + 1/3 \text{O}_2 \rightarrow 1/3 \text{U}_3\text{O}_8$ and $\text{U}_3\text{O}_8 + 9\text{F}_2 \rightarrow 3 \text{UF}_6 + 4 \text{O}_2$.

^d Fluorine utilization efficiency to form UF_6 by the reaction $1/3 \text{U}_3\text{O}_8 + 3 \text{F}_2 \rightarrow \text{UF}_6 + 4/3 \text{O}_2$. Separate values are reported for the efficiency in the specific period and for the cumulative (total) efficiency during the run up to the end of the period.

In general, temperature control was excellent in this run, and bed temperature differentials were about 50 C (except for one period wherein the differential was 75 C). A temperature of 200 C was generally observed at the Monel off-gas filter in the disengaging section. In one short period, however, the temperature reached 330 C. This temperature of 330 C was higher than in earlier runs and is taken to indicate a relatively large amount of elutriated fines, which were fluorinated in the disengaging section. At the conclusion of the run, inspection of the interior

of the disengaging section showed that a layer of fines remained. A separate fluorination at 200 C was used to remove these fines, and yielded 600 g of uranium hexafluoride. Subsequent inspection of the disengaging section showed the absence of a layer of fines.

Temperatures above 200 C at the filter are considered undesirable because of possible damage to the porous metal filter by fluorination. Although cooling can be provided for the filters (as in a new fluorinator being built), it is not certain how effective such cooling will be if a substantial amount of fluorination of uranium oxide fines can take place in the filter chamber. Thus, the prevention of such heavy elutriation of fines to the filter chamber is considered highly desirable.

A second two-zone run (Run UOF-62) was made with an 8.8-kg batch of $\frac{1}{2}$ -in. pellets. In this run, a lower fluidization gas rate (0.9 ft/sec at the pellet zone) and a smaller Alundum bed (5.4 kg) was used. These changes were intended to increase freeboard and reduce elutriation of fines from the upper zone. Operation was at 500 C and was generally similar to Run UOF-61, except that mechanical vibration was maintained during most of the run. The pellet charge was the same type and amount as in Run UOF-61.

The production rate obtained in Run UOF-62 is given in Figure 55, and the operating conditions and results are summarized in Table 30. No definite trend of uranium hexafluoride production rate was observed during the run. The average production rate was about 30 lb uranium hexafluoride/(hr)(sq ft), and the average fluorine efficiency was 54 percent. However, temperature control and fluidization quality were not good in this run. Temperatures were low in the pellet zone, and incipient temperature surges were noted at the control point near the fluorine introduction

Figure 55

URANIUM HEXAFLUORIDE PRODUCTION RATES.
TWO-ZONE OXIDATION-FLUORINATION OF
URANIUM DIOXIDE PELLETS
(UOF-62)

3-in. Finned Reactor
12-in. Pellet Bed
24-in. Al₂O₃ Fluid Bed (static)
Temperature: 500 C
Once-through Gas Flow

zone at the bottom of the upper zone. The run was terminated in order to observe the bed condition. A substantial quantity of fines (890 g) and pellet remains (500 g) were recovered from the bed. Individual pellet pieces were diminished in size, but retained their original cylindrical shape. A thin layer of oxide fines covered each piece, indicating that oxidation had occurred at the surface. Inspection showed no accumulation of fines in the disengaging section. However, the upper zone of the fluorinator was found to contain a small amount of agglomerated material, apparently containing fines of intermediate compounds of uranium. From its shape, the agglomerated material appears to have formed on a thermowell above the pellet zone. It is likely that this formation occurred on the control thermowell and was the reason for the poor fluidization quality. Also, it appears likely that this formation occurred in the second period of the run (see Table 30), in which high fines production and essentially complete reaction of fluorine were observed.

Table 30

OPERATING CONDITIONS AND RESULTS OF TWO-ZONE OXIDATION-
FLUORINATION OF URANIUM DIOXIDE PELLETS
(Run UOF-62)

3-in. Finned Reactor

Temperature: 500 C

Overall Fluorine

Efficiency: 54 percent

UO₂ Charge: 8.8 kg (12-in. bed of
 $\frac{1}{2}$ -in. pellets)

Al₂O₃ Charge: 5.4 kg

Run Time (hr)	Gas Flow in Pellet Bed		Gas Flow in Alundum Bed			Avg Fluorine Efficiency ^c in Period (%)	Avg UF ₆ Production in Period [lb/(hr)(sq ft)]
	u _f ^a (ft/sec)	O ₂ (%)	u _f ^a (ft/sec)	O ₂ (%)	F ₂ (%)		
0.5-2	0.9 ^b	4.1	1.0	3.6	12.8	56	30
2.5-3.5	0.8	5.3	1.0	4.7	12.7	92	49
3.5-5.5	0.9	5.6	1.15	5.0	11.0	39	21
7-9.5	0.9	6.0	1.15	6.3	11.1	54	35
11-12	0.9	7.4	1.2	6.4	13.4	26	17
12-13	0.95	12.5	1.2	11.0	12.7	47	31

^aSuperficial fluidization velocity based on empty column at operating conditions.

^bTemperature, 500 C.

^cFluorine utilization efficiency to form uranium hexafluoride product by reaction $\frac{1}{3} \text{U}_3\text{O}_8 \rightarrow \text{UF}_6 + \frac{4}{3} \text{O}_2$.

Discussion of Two-zone Runs

A comparison of the results obtained in the two-zone Runs UOF-61 and UOF-62 indicates that the runs behaved in a manner which is consistent with the assumed model for the mechanism of cake

formation. In the first run, results were quite satisfactory. In the second run (UOF-62), the gas flow rate through the pellet bed was 0.8 to 0.9 ft/sec. It is possible that this flow rate was too low to provide satisfactory elutriation of fines from the pellet bed. In this case, it is possible that substantial amounts of accumulated fines could break through periodically into the upper zone, thereby producing temperature surges and caking. Such an explanation would account for the unusually high fluorine efficiency (92 percent) observed during the period between 2.5 and 3.5 hr in Run UOF-62 (see Table 30). Further tests are planned with the aim of establishing better control of the oxidation and elutriation.

Comments on Runs to Date

In Table 31, data are given concerning the runs which to date appear most promising for practical process application. The selection includes the runs which were carried to satisfactory conclusion, without caking, and under well-controlled operating conditions. Brief descriptions of type of charge and conditions of gas flow are given. The overall average rates of production of uranium hexafluoride and fluorine utilization efficiencies are also given. The average values of production rate and fluorine efficiency do not indicate the maximum values attained nor do they represent the final optimum values. This is particularly true in the case of the batch runs. Batch Run UOF-61, for example, showed a rate of 70 lb uranium hexafluoride/(hr)(sq ft) during a significant portion of the run. Also, fluorine efficiency could be increased in practice by using gas recycle.

Table 31

DIRECT FLUORINATION PROCESS STUDIES: CONDITIONS IN RUNS FREE FROM CAKING

Run No.	Fuel Charge	Gas-flow Scheme	Average Gas Comp	Average Production Rate [lb UF ₆ /(hr)(sq ft)]	Average F ₂ Efficiency (%)
UOF-34	Batch; initial 6-in. bed height	Full recycle	F ₂ , 40%; O ₂ , ~50%	50	62
UOF-54	Batch; initial 18-in. bed height	Partial gas recycle	Inlet F ₂ , 5%; Inlet N ₂ , 5%; Gas Recycle, 90% (O ₂ , 1-2%)	17	78
UOF-59	Continuous; constant 6-in. bed height	Once-through gas flow	Inlet F ₂ , 20%; Inlet O ₂ , 5%; Inlet N ₂ , 75%	37	54
UOF-61	Batch; initial 12-in. bed height	Once-through gas flow; two-zone operation	Pellet zone: O ₂ , 3-7%. Upper zone: F ₂ , 10%	33	61

From the results presented in Table 31, it appears that the highest rates of production are most likely to be attained in continuous-feed

(shallow pellet bed) runs or in two-zone runs. The form in which continuously fed uranium dioxide is charged is not likely to be critical: rods, pellets, or fragments could all be reduced quickly to U_3O_8 powder within the reactor, or they could be pre-oxidized before introduction. However, work to date has been limited to the use of a single-vessel scheme rather than a pre-oxidation scheme, and emphasis has been placed on batch rather than continuous processes. It is believed that the two-zone scheme is currently most promising for deep-bed batch runs. It is possible that depths in excess of 18 in. can be handled by simple baffles or by gas pulsing to improve fluidization quality in the pellet bed voids. In any event, even a 6-in. limit of bed height would allow a one-foot-diameter reactor to handle a 100-kg pellet batch. If the rate obtained in UOF-34 (see Table 31) is assumed, about three such 100-kg batches could be processed in a 24-hr period. This processing rate, if achieved, is sufficient to process the discharged fuel of six reactors such as the one at Dresden, Illinois.

Design and Construction of Plutonium Facility
(G. J. Vogel, E. Carls, L. Marek, and W. Murphy)

A High-Alpha Engineering Facility is being installed. The installation is being made for pilot plant-scale studies of the fluorination of uranium-plutonium oxide reactor fuel materials in a fluidized bed reactor. Later, equipment will be added to study methods for the separation of the uranium from the plutonium. Fission products can be investigated also at gamma levels that allow direct personnel access. The principal features of the facility were outlined in the previous Quarterly (ANL-6569, page 110).

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

A fluidization-volatility process scheme for the recovery of uranium from enriched uranium-zirconium alloy nuclear fuels is being investigated. This process involves a chlorination of the alloy while submerged in an inert fluidized bed and a subsequent fluorination step. During the chlorination step, the zirconium is separated from the alloy as the tetrachloride (sublimation point, 331 C at 14.7 psia), leaving particulate uranium chlorides in the reactor assembly. The uranium is volatilized as uranium hexafluoride (sublimation point, 56.5 C at 14.7 psia) and recovered during the fluorination step.

The overall objective of this work is to develop a high-decontamination, high-uranium recovery (~99 percent) process which will offer decided advantages over the currently employed process of solvent extraction. Among the advantages of volatility processes are (1) substantial reduction in the quantity and type of radioactive wastes (dry solids result instead of large volumes of liquid waste); (2) the product form is uranium

hexafluoride, immediately available for isotope enrichment; (3) the number of process steps are few, thereby reducing capital expenditures; and (4) reprocessing of short-cooled (higher levels of activity) fuel is believed feasible since no radiation damage to reagents occurs as in solvent extraction work. This thereby reduces inventory costs. The process on a pilot-plant scale will be demonstrated in a facility which is scheduled for installation toward the end of this year. Major items for the pilot plant (see ANL-6543, page 153) have been received. These include the two fluid-bed units, the primary reactor and hydrolysis column, special high-temperature valves, and the panelboard complete with instruments. The pilot-plant studies will be made with nonirradiated fuel material.

Currently, studies of the effects of process variables on uranium recovery are in progress in a bench-scale ($1\frac{1}{2}$ -in.-diameter) unit. Also, in this work, a static bed of inert granular material (Norton Alundum) is being evaluated for use as a high-temperature filter. This filter serves to retain uranium particulate solids formed during chlorination of the alloy as well as other fine particles entrained by the off-gas from the reactor. The Alundum used in the filter bed is the same as that used in the reaction bed. A less costly grade of Alundum (Norton, type 38 versus type RR) was tested, both as the fluid-bed and static-bed material.

The work is evaluated primarily on the basis of the uranium material balance, that is, the quantity of uranium retained by the inert bed material after chlorination and fluorination, the quantity of uranium hexafluoride recovered in the cold traps, and the quantity of uranium lost to the off-gas streams. In previously reported studies (see ANL-6413, page 138) on the chlorination step in which only hydrogen chloride was used as the initial reactant, uranium losses through the static-bed filter were about 0.2 percent of the initial charge. For the overall cycle, less retention of uranium by the inert solids (Alundum) was noted with the use of greater quantities of hydrogen chloride (in the range of 4 to 25 times the stoichiometric requirements based on the zirconium in the original alloy charge) and also with higher fluorine temperatures (500 C as compared to 400 C). Values of uranium retention as low as 0.8 percent were attained. In work with other chlorinating agents, it was found that the use of phosgene after hydrochlorination appeared to give a further improvement with respect to the removal of uranium from the inert solids. Overall uranium retention was as low as 0.2 percent of the uranium initially charged (see ANL-6569, page 116). This value corresponds to a final uranium concentration in the Alundum bed of about 0.01 weight percent. At the present time, however, it is not known whether phosgene will be necessary in the processing scheme.

Additional studies with phosgene were made in which a mixture of hydrogen chloride and phosgene was used as the initial reactant. Identification was made by infrared spectrophotometric analysis of several

compounds collected in the uranium hexafluoride cold traps. It is suspected that some of these compounds may have contributed to the unexpected ignitions which occurred when the cold traps were vented in the runs in which phosgene-hydrogen chloride mixtures were used (see ANL-6569, page 117). Results of this work are reported below.

In related process studies, vapor-deposition techniques are being employed in a continuing investigation of the pyrohydrolysis of zirconium tetrachloride to the dioxide in a fluid-bed reactor (of 6-in. diameter) as part of a scheme for the disposal of the off-gas from the hydrochlorination step. This investigation is directed towards finding operating conditions, such as temperature, steam excess, and fluidizing gas rate, which will give maximum deposition of product oxide on the granular bed material.

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

Chlorination and fluorination studies with low uranium-zirconium alloy are being carried out in a prefluorinated, $1\frac{1}{2}$ -in.-diameter nickel (Type "A") reactor containing a fluidized bed of prefluorinated Alundum (Norton Company). The gas stream from the reactor is led to a down-flow Alundum bed filter (of 1.5-in. diameter) wherein particulate solids entrained from the fluidized bed reactor are collected. The effluent gases are cooled to condense the volatile products, which are then treated and disposed of. Details of the apparatus and the experimental procedure were reported last quarter (see ANL-6569, pages 114 to 115).

In the current work, a mixture of hydrogen chloride and phosgene was used as the initial reactant. Hydrogen chloride readily attacks the alloy, whereas the phosgene is expected to chlorinate oxides (primarily of zirconium) which are believed to increase uranium retention in the bed. Chlorination with the hydrogen chloride-phosgene mixture was followed by a second chlorination in which phosgene alone was employed. After the two chlorination steps had been completed, the material remaining in the reactor was fluorinated. Two runs were made with this reaction sequence.

The fuel charge consisted of 240 g of 51 weight percent uranium-Zircaloy alloy chips. The reaction bed consisted of 320 g of -40 +60 mesh Alundum, Type RR in one run (Run 29) and Type 38 in the other (Run 30). The temperatures in the reactor and in the filter section were maintained at 400 C throughout the cycle except during the final 2 hr of fluorination in Run 30, when the temperatures were raised to 500 C. Conditions and results of these runs are summarized in Table 32. A previous run (Run 28) is also presented for comparison.

Table 32

CHLORINATION-FLUORINATION REACTION STUDIES ON URANIUM-ZIRCALOY ALLOY

Equipment: 1-1/2-in. column (down-flow filter for Run 30 only)
 Alloy Charge: 240 g of 5.1 w/o uranium-Zircaloy alloy chips (1/8-1/4-in. size)
 Inert Bed Charge: 320 g of Alundum, -40 +60 mesh (Norton Company)
 Temperature: 400 C except 500 C during final 2 hr of Runs 28 and 30

Run No.	Alundum Type	Reaction Period 1		Reaction Period 2		Reaction Period 3		Reaction Period 4 Time ^{b,c} (hr)	Residual Uranium	
		Time (hr)	(Times Stoich) ^a	Time (hr)	(Times Stoich) ^a	Time (hr)	(Times Stoich) ^a		(w/o in Fluid Bed)	(% of U Initially in Charge)
28 ^d	RR	7	4	-	-	5.2	7	7	0.05	1.3
								9	0.03	0.8
								11 ^e	<0.01	<0.2
29	RR	-	-	5	3.75	3	4.25	1.7	0.04	1.0
								7.0	0.04	1.0
30	38	-	-	4.8	3.75	1.7	1.25	2.5	0.03	0.8
								4.5 ^e	0.02	0.5

^a Stoichiometric amounts based on original alloy charge according to the reaction $\text{Zr} + 4 \text{HCl} \rightarrow \text{ZrCl}_4 + 2 \text{H}_2$.

^b Cumulative time.

^c Fluorine excess was about 20 times stoichiometric per hour, based on uranium initially in charge.

^d Reported previously in ANL-6569, page 116.

^e Final 2 hr at 500 C.

Effect of Phosgene on Retention of Uranium by the Inert Bed Material. When the 4:1 mixture of hydrogen chloride and phosgene, followed by phosgene, was used (as in Runs 29 and 30) instead of hydrogen chloride alone followed by phosgene (as in Run 28), shorter reaction times and lesser quantities of chlorinating agents were required to reach comparable residual uranium values in the Alundum fluid bed. Analyses (see Table 32) of Type RR Alundum beds showed that in Run 28 the residual uranium value was 0.05 weight percent for an overall cycle time of 19.2 hr and 11 times the stoichiometric chlorination reactant requirement, whereas in Run 29 the residual uranium value was 0.04 weight percent for the much shorter cycle time of 9.7 hr and eight times the stoichiometric chlorination reactant requirement. In Run 30, in which the less costly Type 38 Alundum was used, the residual uranium value was 0.03 weight percent for a cycle time of 9 hr and five times the stoichiometric chlorination reactant requirements. This residual uranium value is quite similar to the value obtained in Run 29 in which the high-purity Type RR Alundum was used. The analytical values reported here are accurate to better than five percent of the given values, so that the differences noted are considered significant. Extended fluorination at 400 C, as in Run 29, did not give further uranium removal. However, increasing the temperature of fluorination to 500 C with either bed material (RR or Type 38 Alundum) did result in additional uranium removal. The best result, <0.01 weight percent residual uranium which corresponded to <0.2 percent of the initial charge, was achieved with the RR Alundum.

As can be seen from these data, both the reaction cycle time and quantities of reactants have been reduced considerably over those found in the earlier work. The high excess of fluorine (~20 times stoichiometric per hour based on uranium charge) in these studies is not of serious consequence, since in practice it is planned to recycle the gas.

When Type 38 Alundum was used, no problems were experienced in the fluidized bed, but excessive pressure built up across the static filter bed during both the chlorination and fluorination steps. Upon examination of the filter bed after the run, the middle portion was found to be caked (possibly because of a sintering action) and a layer of fine (-325 mesh) particulate solids was found deposited in the top portion of the bed. Since both the fluid bed and the filter bed are composed of relatively coarse material (-40 +60 mesh Alundum and -14 +20 mesh Alundum), the fines probably resulted from the attrition of fluid-bed particles and were carried to the filter section by the gas stream. The source of the fines is confirmed by the high aluminum content of the fines, as shown in the spectrochemical analysis below:

<u>Element</u>	<u>Percent</u>	<u>Element</u>	<u>Percent</u>
Al	>>10	U	<1
Na	1-10	Ni	~0.5
Zr	~1		

The caking in the filter bed may be due to chemical reaction between the gases and the impurities (primarily sodium: ~0.2 percent, and iron: ~0.03 percent) in the Type 38 Alundum. A lower temperature of the filter bed may offer some relief from caking. However, if the fluid-bed material undergoes severe attrition and excessive fines are produced during fluidization, the benefits derived from the use of a lower filter-bed temperature may be nullified, and it may be necessary to discontinue the use of Type 38 Alundum in future work.

Effect of Phosgene on Uranium Losses during Chlorination.

Current results on uranium losses through the filter bed during the chlorination step indicate that the use of the hydrogen chloride-phosgene mixture followed by the use of phosgene alone has given greater losses (about 5 percent) than those resulting from the use of hydrogen chloride alone. In these latter experiments (see ANL-6543, page 150), typical losses were <0.2 percent. In each run, the temperatures of the filter bed and the reaction bed were maintained at the same level, 400 to 450 C. The higher losses when phosgene is used may be caused by either the formation of smaller particles which are not readily filterable or by the formation of higher, more volatile chlorides (for example, uranium hexachloride, b. p. 372 C).²⁸ If the latter is the case, lower temperatures for the fluid

²⁸ Extrapolated value given in Stoller, S. M., and Richards, R. E., Reactor Handbook, Vol. 2, 2nd Edition, Interscience Publishers, New York (1961), p. 267.

bed and filter bed may be of some benefit. Although it is not feasible to lower the bed temperatures radically because this might result in the condensation of the zirconium tetrachloride, the effect of decreasing the temperature to about 350 C will be studied in future experiments.

Analysis of Material in Cold Traps. In the current experiments in which a mixture of hydrogen chloride and phosgene was used as the initial reactant, ignitions of the material in the cold traps used for the collection of uranium hexafluoride occurred after the fluorination step. The cold traps consisted of a series of three coils maintained at the sublimation point of dry ice (~ -80 C) by immersion in a trichloroethylene-dry ice bath. The ignitions occurred on two successive days during Run 29, first when the traps were vented preparatory to nitric acid hydrolysis of the condensed uranium hexafluoride, and later during the actual hydrolysis step.

In order to investigate the cause of the ignitions, a run (Run 30) was made under conditions that nearly duplicated Run 29 with regards to time and quantities of reactants. The gases condensed in the cold traps were then analyzed by infrared spectrophotometric techniques, each cold trap coil being checked separately. The material in each of the coils was also subsequently hydrolyzed and analyzed by wet methods.

The results of the infrared analyses, carried out by Dr. M. J. Steindler and Mr. W. H. Gunther of the Volatility Laboratory Group, are summarized in Table 33. Specific compounds identified in each of the traps (Trap 1 being closest to the reactor assembly) at two temperatures are noted as well as the absence of a number of compounds. Tentative, if not positive, identifications were made of uranium hexafluoride, chlorine trifluoride, and chlorine dioxide. Some unidentifiable material (Compound X, Table 33) was present in the region of wave numbers between 535 and 560 cm^{-1} .

The results of the analyses of the hydrolyzed trap material are presented in Table 34 in a way which shows the effect of various chlorinating treatments on the composition of the material found in the cold traps. This method of presentation may also aid in explaining the ignitions. Using the uranium content as a basis and assuming that the uranium, zirconium, and chlorine are present as the hexa-, tetra-, and tri-fluorides, respectively, there appears to be a large excess of fluorine only in Run 30, in which the hydrogen chloride-phosgene mixture was used followed by phosgene. Thus, a fluorine-containing compound may be associated with the ignitions. This compound may or may not be the unidentifiable material found in the course of infrared analysis. In Run 30, the chlorine-to-uranium ratio of the material in the cold traps also was appreciably higher than in the run in which hydrogen chloride was used alone (Run 26) or in the run in which chlorination with hydrogen chloride was followed by chlorination with phosgene (Run 28).

Table 33

SUMMARY OF IDENTIFICATION OF MATERIAL IN TRAPS FROM
RUN 30, BASED ON INFRARED DATA

	Trap 1 ^a		Trap 2 ^a		Trap 3 ^a
	0 C	Room Temp	0 C	Room Temp	Room Temp
Present ^b	UF ₆ Compound X	UF ₆ Compound X	- Compound X	UF ₆ , ClF ₃ Compound X	- Compound X
Probably present ^c	ClF ₃	ClF ₃	UF ₆ , ClF ₃	-	UF ₆ , ClO ₂
Possibly present ^d	ClO ₂	ClO ₂	ClO ₂ , ClO ₃ F COClF, NOF	ClO ₂ , ClO ₂ F	-
Probably absent ^e	ClO ₂ F, C ₃ F ₈ C ₄ F ₁₀	ClO ₂ F, C ₃ F ₈ C ₄ F ₁₀	COCl ₂ , COF ₂	COClF, C ₃ F ₈ , C ₄ F ₁₀	ClF ₃ , ClO ₂ F
Absent ^f	NF ₃ , NOF, N ₂ F ₄ , COClF, HF, ClO ₃ F, COF ₂ , COCl ₂ , Cl ₂ O	NF ₃ , NOF, N ₂ F ₄ , COClF, HF, ClO ₃ F, COF ₂ , COCl ₂ , Cl ₂ O	NF ₃ , Cl ₂ O, N ₂ F ₄ , HF, C ₃ F ₈ , C ₄ F ₁₀ , ClO ₂ F	NF ₃ , NOF, N ₂ F ₄ , HF, ClO ₃ F, COCl ₂ , Cl ₂ O, COF ₂	NF ₃ , NOF, N ₂ F ₄ , COClF, C ₃ F ₈ , C ₄ F ₁₀ , HF, ClO ₃ F, Cl ₂ O, COCl ₂ , ClO ₃ F, COF ₂

^aTrap 1 is the first trap downstream from the fluid-bed reactor assembly. The traps were sampled at the indicated temperatures.

^bIdentification of compounds reasonably certain, and presence of Compound X in region of 535 to 560 cm⁻¹ is indicated.

^cIdentification based on one or two principal peaks.

^dIdentification based on presence of weak peaks.

^eIdentification based on absence of some important peaks.

^fIdentification based on absence of important peaks.

Table 34

EFFECT OF CHLORINATION TREATMENT ON THE CONTENTS OF THE
URANIUM HEXAFLUORIDE COLD TRAPS

Types of Cold Traps: Two copper and one nickel coil in series immersed in a dry ice-trichloroethylene bath

Run No.	Reactants during Chlorination	Mole Ratio of Individual Components to Uranium in the Cold Traps			Calculated ^a Total F ₂ /U
		Zr/U	Cl ₂ /U	Total F ₂ /U	
26	HCl alone	0.03	0.02	3.4	3.1
28	HCl followed by COCl ₂	0.002	0.02	3.4	3.1
30	HCl-COCl ₂ mixture followed by COCl ₂	0.08	0.27	11.1	3.4

^aThe total amount of fluorine calculated from the analytical values of U, Zr, and Cl assuming that these were present as UF₆, ZrF₄, and ClF₃, respectively.

Analysis of the fluid bed after chlorination in Run 29, in which the hydrogen chloride-phosgene mixture was used, showed a carbon content of 0.17 percent. It has been suggested that this carbon may have been a contributing factor in the ignitions. This, however, appears unlikely. Although carbon may have reacted during the fluorination, it is probable that the reaction products (such as CF_4 and C_3F_8) passed through the cold traps, and therefore could not have contributed to the ignitions.

Future Work. In future studies, a hydrofluorination step will be conducted prior to the fluorination step in order to remove the chlorine from the bed before the cold traps are put into use. Further procedural changes are being tested which will permit the uranium hexafluoride collected in the cold traps to be hydrolyzed without exposing the hexafluoride to air. These changes are expected to avoid the conditions which led to the halogen ignitions. Studies without phosgene are being resumed to obtain comparative data in the hope that these will indicate that phosgene need not be used in the process.

Overall objectives are the solution of operational problems and the consistent achievement of uranium recoveries higher than 99 percent. Studies of the effects of varying the following items on the recovery of uranium are planned:

- (1) temperature of fluid bed during (a) hydrochlorination, (b) chlorination, (c) hydrofluorination, and (d) fluorination;
- (2) temperature of filter bed during steps a, b, c, and d;
- (3) time of reaction during steps a, b, c, and d;
- (4) excess of reactant during steps a, b, c, and d;
- (5) hydrogen and chlorine feed instead of hydrogen chloride feed;
- (6) successive chlorinations of fresh charges of the uranium-zirconium alloy prior to hydrofluorination and fluorination;
- (7) Zircaloy with lower percentage of uranium;
- (8) addition of simulated fission products to the system;
- (9) shape of Zircaloy (long strips in distinction to the chips which are being used at present);
- (10) weight ratio of Zircaloy to Alundum;
- (11) particle size and quality of Alundum in the fluid bed and in the filter bed;
- (12) gas-stream temperatures in the cold traps during the fluorination;
- (13) sodium fluoride traps for recovery of uranium hexafluoride; and
- (14) corrosion of the nickel equipment.

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

The pyrohydrolysis of zirconium tetrachloride is being studied for the purpose of developing a scheme for the disposal of waste tetrachloride produced by the chlorination of uranium-zirconium alloy fuels. In this work, the tetrachloride is converted to the more easily stored oxide by reaction with steam in a fluidized bed. It has previously been shown (see ANL-6569, pages 118 to 121) that the hydrolysis can be carried out at relatively low tetrachloride feed rates (~ 2.2 kg/hr). The difficulty of pressure buildup, which was caused by the collection of fines on the exit gas filters, appears to have been eliminated by increasing the filter blowback pressure (to 80 psig from the original 30 psig). However, a significant proportion of the product oxide has been found in the form of fine material (~ 200 mesh). The quantity of fines which is formed is a measure of the efficiency of the deposition of oxide on the fluidized solids. Recent effort has been devoted to finding operating conditions which will increase the extent of deposition, and at the same time allow operation at higher feed rates.

The experimental details for the latest runs are given in Table 35. The equipment, unchanged from that previously described

Table 35

FLUID-BED HYDROLYSIS OF ZIRCONIUM TETRACHLORIDE:
RUN CONDITIONS AND RESULTS

Equipment:		6-in.-diameter fluidized bed				
Bed Material:		refractory-grade Alundum, nominal grade 90 mesh ^{a,b}				
Initial Bed Weight:		16 kg				
Blowback Pressure:		80 psig				
Fluidizing Gas Flow Rate:		2.5 scfm ^c				
Run No.	Run Duration (hr)	ZrCl ₄ Feed Rate (kg/hr)	Steam Rate (x Stoich)	Bed Temp (C)	Increase in Pressure Drop (in. Hg)	Proportion of Fines in Final Bed (%)
CO-27	6	1.8	5.3	350	0.3	6.8
CO-28 ^e	6	0	- ^e	350	0.1	5.2
CO-29	3 $\frac{1}{4}$	2.5	2.9	350	1.0	7.9
CO-30	2 $\frac{1}{2}$	3.2	2.1	300	0	27.6
CO-31	3 $\frac{1}{2}$	2.3	3.1	250	1.8	9.4
CO-32	3	3.3	3.7	350	0.1	15.9
CO-35	3	2.6	2.8	350	0.4	7.7

^aAlundum coated with ZrO₂ used in CO-28 and CO-30.

^bNominal 60 mesh material in CO-35.

^c3.0 scfm in CO-35.

^dIncludes fines collected on the filters.

^eAn attrition run with no ZrCl₄ fed, but the same steam rate as for CO-27.

(see ANL-6569, pages 118 and 119), incorporates a vibrating screw feeder which supplies solid zirconium tetrachloride to a sublimation furnace, whence the vapor is carried in a stream of nitrogen into the fluidized bed. This gas stream also serves as the fluidizing medium. The main experimental changes from previous work were:

- (1) increased feed rate from 2.2 to 2.5 kg/hr and reduced steam excess from 3.5 to 2.9 times the stoichiometric requirements in Run CO-29;
- (2) reduced bed temperatures in Runs CO-30 and -31 (300 and 250 C, respectively; previous temperatures up to 450 C);
- (3) further increase in feed rate to 3.3 kg/hr in Run CO-32; and
- (4) larger particle size in the starting bed in Run CO-35 (nominal 60 mesh as compared to 90 mesh).

In addition, a relatively long run of 6 hr (Run CO-27) was made under conditions established previously as being satisfactory, and a base-line run was made with no tetrachloride feed to provide data on the quantity of fine material (-200 mesh) obtained from attrition of the bed particles. The extent of product deposition was evaluated on the basis of the pressure buildup in the column (fines on the filters) and by the proportion of the final bed found as fines.

Results and Discussion. The proportion of fine material (-200 mesh) found in the bed and on the filters in the base-line attrition run (CO-28) was about five weight percent of the final bed. Subsequent runs were thus compared in terms of the basis of the amount of fine material produced in excess of about five percent. Since the runs were of varying duration, a time factor was considered also. A greater amount of fine material than was produced by attrition was produced in all runs. The increased feed rate and reduced steam rate as in Runs CO-29 and -35 seemed to cause a moderate increase in fines production, a total of about eight percent fines produced in about 3 hr as compared with seven percent fines produced in 6 hr in Run CO-27, in which a lower feed rate and higher steam excess were used. The coarser starting-bed material which was used in Run CO-35 appeared to have no effect.

A further increase in tetrachloride feed rate (from 2.4 to 3.3 kg/hr) in Run CO-32 resulted in a much greater quantity (~16 percent in 3 hr) of fine material being produced. Runs CO-30 and CO-31 were intended to allow comparison of the effect of reduced bed temperature. However, an unexpectedly high feed rate in Run CO-30, which was caused by a change in the screw-feeder behavior, prevented a proper comparison. The high feed rate (3.2 kg/hr) effected a high rate of fines production. The effect of bed temperature, as indicated by comparing Runs CO-29 and -31,

appears to be the production of more fine material at the lower temperature. In this series of runs with the high blowback pressure (80 psig), the effect of fines on the pressure drop across the exit gas filters has remained negligible.

It will be necessary in future work to examine further the effect of high tetrachloride feed rates on the process and to determine the maximum capacity of the apparatus. Other effects still to be studied include the use of finer material in the starting bed, higher bed temperatures, and hydrogen chloride as a major component of the carrier gas.

Absorption of Zirconium Tetrachloride on Solid Sodium Chloride (J. Barghusen)

In the processing of zirconium-uranium alloy fuels, the separation of zirconium from uranium is achieved by volatilization of zirconium tetrachloride formed by reaction of the alloy with hydrogen chloride. The gaseous zirconium tetrachloride must be collected in a form suitable for ultimate disposal. A series of exploratory tests has been made to ascertain whether a solid absorbant for zirconium tetrachloride could be employed to recover this material from the process gas stream.

The solid absorbant employed in these tests was rock salt of +8 mesh particle size. The reaction between zirconium tetrachloride and sodium chloride to produce sodium chlorozirconate may be represented by the equation $\text{ZrCl}_4 + 2 \text{NaCl} \rightarrow \text{Na}_2\text{ZrCl}_6$. Evaluation tests were made by passing a dilute gas stream of zirconium tetrachloride in nitrogen through a heated bed of rock salt and analyzing the zirconium tetrachloride content in the off-gas. A schematic diagram of the equipment is shown in Figure 56. The absorber consisted of a 2-in.-ID nickel pipe, 12 in. long,

Figure 56

EQUIPMENT FOR EVALUATING ABSORPTION OF ZIRCONIUM CHLORIDE ON A STATIC BED OF SODIUM CHLORIDE

containing approximately 925 g of rock salt supported on a perforated plate. Unreacted zirconium tetrachloride in the gas stream leaving the absorber was collected in an ambient-temperature condenser and aqueous scrubber. Analyses of the condensed material and scrub solution provided an estimate of the quantity of zirconium tetrachloride which passed through the absorber.

The extent of zirconium tetrachloride absorption on sodium chloride was studied at temperatures of the absorber bed ranging from 250 to 460 C. The zirconium tetrachloride in the nitrogen carrier gas ranged from 0.65 to 2.0 volume percent. Run time varied from 2 to 4 hr.

The results of three experiments are presented in Table 36. In Run No. 1, which was made at a bed temperature of 350 to 400 C, an absorption of about 80 percent of the zirconium tetrachloride was achieved. A significantly higher degree of absorption, 98 percent, was achieved in Run No. 2, which employed bed temperatures of 250 to 320 C. Severe agglomeration of the rock salt bed occurred in Run No. 3, which was carried out at a bed temperature of 450 C. A similar occurrence was experienced at ORNL,²⁹ which reported severe "fusion" of the sodium chloride particles at a bed temperature of 480 C.

Table 36

ABSORPTION OF ZIRCONIUM TETRACHLORIDE IN A PACKED BED
OF SODIUM CHLORIDE

Absorber: 2-in.-ID nickel pipe, 12 in. long
Bed Material: 900 to 930 g of rock salt, +8 mesh particles
Nitrogen Gas Rate: 0.45 scfm

Run Number	Bed Temperature (C)	Run Duration (hr)	Total ZrCl ₄ Fed to Absorber (g)	ZrCl ₄ Concentration		ZrCl ₄ Absorbed (%)
				Inlet (vol %)	Outlet (vol %)	
1	350-400	2	183	1.25	0.26	80
2	250-320	2	200	1.37	0.02	98
3	450-460 ^a	2	297	2.03	0.33	84

^aAgglomeration of sodium chloride particles occurred.

The results from Run No. 2, in which a 98 percent absorption of zirconium tetrachloride was achieved, also indicate that it is possible to reduce the concentration of zirconium tetrachloride in a gas stream to values as low as 0.02 volume percent. Since no sodium was detected in

²⁹Chemical Technology Division, Monthly Progress Report for December 1957, ORNL-2468 (April 1958), pp. 11-12.

either the condenser or the scrub solution, the zirconium that left the absorber left in the form of zirconium tetrachloride vapor rather than particulate sodium chlorozirconate.

Examination of the final beds showed that the sodium chlorozirconate product is formed on the surface of the sodium chloride particles. This yellow-colored layer readily flakes away from the surface to form fine particulate solids, mainly minus 60 mesh.

It is apparent from the results of these tests that zirconium tetrachloride may be efficiently absorbed from a gas stream by reaction with sodium chloride in a static-bed system, and that common rock salt appears to be an acceptable grade of sodium chloride for this purpose. However, considerable work would be required to optimize the process conditions.

C. Conversion of Uranium Hexafluoride to Uranium Dioxide:
Preparation of High-density Particles
 (I. Knudsen, N. Levitz, M. Jones)

Process-development studies were continued on a direct fluid-bed scheme for preparing high-density uranium dioxide particles from uranium hexafluoride. The scheme involves the simultaneous reaction of the hexafluoride with steam and hydrogen in the region from 650 to 700 C. The dense, spheroidal uranium dioxide product would be intended for use in dispersion or packed fuel elements.

In previous work (see ANL-6569, pages 121 to 124), particles of varying densities were produced when the concentration of steam in the reactant feed stream was varied. The highest densities (up to 86 percent of theoretical density as measured by mercury displacement) were obtained at steam concentrations corresponding to the range from 0.75 to 1.4 times the stoichiometric requirements.* Lesser amounts of steam (to 10 percent of stoichiometric) gave lower densities. In current work, the effect of bed temperature and hexafluoride feed rate, and of duration of feed interval were investigated; additional tests of the effect of steam concentration were also carried out. Unexpectedly, the hexafluoride feed-nozzle position (that is, the length extending upward into the fluidized bed) was found to be significant and runs made with the nozzle in two positions are discussed. Results of sintering tests** performed in a hydrogen atmosphere on samples of dioxide product are also discussed.

The studies are being conducted in a 3-in.-diameter cone-bottom Monel column described previously (see ANL-6379, page 183). The run

*Based on the reaction $\text{UF}_6 + 2\text{H}_2\text{O} + \text{H}_2 \rightarrow \text{UO}_2 + 6\text{HF}$.

**The sintering tests were carried out by the Ceramics Group of the ANL Metallurgy Division.

procedure involves alternating periods of uranium hexafluoride feed with periods of residual fluoride cleanup when only steam and hydrogen are fed. In some cases, a greater steam rate was used during the cleanup period than during the hexafluoride feed period in order to achieve consistently a fluoride content below 300 ppm in the uranium dioxide product. The hydrogen rate was kept relatively high at 10 to 20 times the stoichiometric requirement. Product was removed semicontinuously (after each cleanup period) so that the bed weight remained approximately constant (~6 kg or about 8-in. static height). Sufficient seed particles, about 160 μ in diameter, were added to maintain the average bed particle size between 325 and 350 μ . Run periods ranged from 6 to 21 hr, usually just sufficiently long to determine product density effects.

Results

Uranium dioxide with densities of 9.7 to 9.8 g/cc (nearly 90 percent of theoretical density) was produced in a run at 700 C with a steam rate of 1.15 times stoichiometric. Tapped bulk density of the product averaged 7.0 g/cc. Other runs, which were made at 650 C with steam rates over the range from 0 to 1.55 times stoichiometric requirements, resulted in products having densities of 8.0 to 9.5 g/cc. Conditions and results of these runs are summarized in Table 37. In Figure 57, current results and previous data are plotted which show particle density as a function of steam excess and the apparent effect of the position of the hexafluoride feed nozzle.

Table 37

PREPARATION OF HIGH-DENSITY URANIUM DIOXIDE PARTICLES FROM URANIUM HEXAFLUORIDE IN FLUIDIZED BEDS

Equipment:	3-in.-diameter Monel Column
Temperature:	650 C, except 700 C for Run O
Bed Weight and Height:	6 kg, 8-10 in. static
Superficial Velocity:	1.0 ft/sec (based on inlet quantities of steam and hydrogen, and column cross section at run conditions)
Run Procedure:	30-min hexafluoride feed, 30-min cleanup per hour ^a
UF ₆ Nozzle Position:	About 3/4-in. penetration into bed in Runs L and M. In other runs, penetration was 3-3/4 in.

Run No.	Reactant Feed Rate (x Stoich ^b)		UF ₆ Feed Rate (g/min)	Run Duration (hr)	UO ₂ Density (g/cc)	
	Steam	Hydrogen			Tapped Bulk	Particle ^c
L	1.55	18.5	24	18	5.6	8.0
M	1.40	18.5	24	12	5.9	8.5
N	1.35	19.0	23	18	6.6	9.3
	1.30	11.9	34	6	6.4	9.1
O	1.15	16.7	26	21	7.0	9.7-9.8
P	0	20.0	25	6.25	6.1	8.7
	0	17.5	28	6	6.1	8.7
Q	0.4	20.5	24	7	6.0	8.7
	1.1	17.5	25	12	6.5	9.2
	1.15	26.9	17	6	6.7	9.5

^a Feed time of 30 min and cleanup time of 45 min for first portion of Run P, and feed time of 15 min and cleanup time of 30 min for last portion of Run P.

^b Based on the reaction $\text{UF}_6 + 2\text{H}_2\text{O} + \text{H}_2 \longrightarrow \text{UO}_2 + 6\text{HF}$.

^c Mercury-displacement determination.

Figure 57

DENSITY OF URANIUM DIOXIDE PRODUCED BY THE SIMULTANEOUS REACTION OF STEAM
AND HYDROGEN WITH URANIUM HEXAFLUORIDE - EFFECT OF STEAM RATE AND
URANIUM HEXAFLUORIDE NOZZLE POSITION

Run Conditions

650 C, 25 g/min UF_6 for 30 min/hr
(letters indicate run designation.)

For Runs L and M (also for J and K, which have been reported previously) the uranium hexafluoride feed nozzle was withdrawn approximately 3 in. in order to increase residence time of the reactants in the bed. In this position, the nozzle extended only $\frac{3}{4}$ in. into the fluidized bed. As can be seen in Figure 57, the use of this short nozzle resulted in a product of lower density. Typically, Run K, made with the short nozzle, resulted in particles with a density of 9.0 g/cc while Run H, made with the longer nozzle, gave particles with a density of 9.5 g/cc. Run N was made with the longer nozzle at a steam rate similar to that of Run M (1.35 vs 1.40 equivalents) and again higher densities were obtained with the long nozzle, 9.3 g/cc as compared with 8.5 g/cc. This effect is as yet unexplained.

In Run P, the effect of using only hydrogen during the hexafluoride feed period was studied. In this run, the newly deposited layer of solids was believed to be uranium tetrafluoride which was converted to the dioxide when steam was added during the fluoride cleanup step. The density of the product was 8.7 g/cc, appreciably lower than that produced with stoichiometric quantities of steam.

Other apparent effects noted in the current studies were as follows:

- (1) Particle density appears to be a function of feed rate; a higher rate (34 g/min in Run N vs a nominal 25 g/min) resulted in a product of lower density, 9.1 vs 9.3 g/cc, whereas a reduced rate (17 g/min vs 25 g/min for two portions of Run Q) gave a product of higher density, 9.5 vs 9.2 g/cc.

- (2) A shorter uranium hexafluoride feed on-time period (15 min in Run P vs. the usual 30 min) at a uranium hexafluoride feed rate of about 25 g/min resulted in no density change.

In general, the fluoride level of the final product was readily reduced to 200 to 300 ppm in the runs in which stoichiometric or greater quantities of steam were used during the hexafluoride feed period. In those cases where less than the stoichiometric quantity of steam was used at the outset, increased amounts of steam during the clean-up period were required to reach this level.

Characterization of the Dioxide Product

In order to characterize the uranium dioxide product produced in these studies (see Figures 58 and 59), pore size distributions* were

Figure 58

DENSE URANIUM DIOXIDE PARTICLES
AS PRODUCED IN THE FLUID-BED
REACTOR

Run PY-66N, Sample 21
Final Particle Density, 9.3 g/cc
Magnification: 37X

Figure 59

CROSS SECTION OF DENSE URANIUM
DIOXIDE PARTICLES SHOWING
LAYER DEPOSITION

Run PY-66N, Sample 24, Etched 60 sec
with 1 part conc H_2SO_4 , 3 parts 30% H_2O_2

Particle Density, 9.3 g/cc

Magnification: 37X

* Pore size distribution measured on a porosimeter by Armour Research Foundation, Chicago, Illinois.

determined for three representative samples, after which the samples were sintered in hydrogen. Samples with densities of about 8.5, 9.3, and 9.75 g/cc (products of Runs L, N, and O, respectively) were tested. The pore-size measurements indicated that most of the porosity of the samples consisted of pores less than 0.4μ in diameter and a significant number were smaller than 0.06μ . The fine-grained structure of the particles may be seen in Figure 60, a relatively high-magnification (533X) photomicrograph of a cross-sectioned particle. Figure 58 shows the smooth, spheroidal appearance of the particles as produced in the fluid-bed, and Figure 59 shows cross sections of a number of particles and illustrates the uniform manner in which the layers are deposited.

Figure 60

CROSS SECTION OF DENSE URANIUM
DIOXIDE PARTICLE SHOWING
FINE-GRAIN STRUCTURE

Run PY-66-0, Sample 24 (not etched)
Particle Density, 9.7 g/cc
Magnification: 533X

It was hoped that the high-temperature firing (1600 to 1725 C for about $2\frac{1}{2}$ hr) would result in elimination of much of the fine pore structure and produce a more dense material. Such was the case. Final particle densities ranged from about 10.4 to about 10.6 g/cc or from about 95 to 96.5 percent of theoretical density (see Table 38). The sintered particles retained their integrity (that is, looked much like those in Figure 58). These data are very encouraging in that a relatively inexpensive sintering procedure upgrades the fluid-bed material to an extent which may make the material suitable for direct use in bulk form for vibratory-compacted or swaged fuel elements. Compaction tests are being considered for the purpose of providing a better estimate of the potential of this material for its intended use.

Future Work

Further exploratory work on the effect of process variables such as bed height and nozzle position is planned. Attempts will also be made to prepare particles of larger size which are useful for the formulation of mixtures for compacting.

Table 38

RESULTS OF SINTERING TESTS ON DENSE URANIUM
DIOXIDE PARTICLES PRODUCED BY THE FLUID-
BED SIMULTANEOUS REACTION PROCEDURE

Particle Size: -40 +200 mesh

Sintering Atmosphere: Hydrogen (with about 300 ppm oxygen as an impurity)

Sintering Schedule: 20 C to 900 C in about 2 hr,
900 C to 1700 C in about 5 hr,
in the range from 1600 to
1725 C for about $2\frac{1}{2}$ hr.

<u>Run No.</u>	<u>Particle Density (g/cc)</u>	
	<u>Before Sintering</u>	<u>After Sintering</u>
O	9.75	10.6
N	9.0	10.4
L	8.5	10.4

D. Fluid-bed Calcination Studies in Small-diameter Columns
(J. W. Loeding, J. E. Kincinas)

The studies investigating the use of small-diameter, fluid-bed columns in conjunction with the preparation of nuclear-critical material have been indefinitely suspended because of increased man-power requirements in other divisional programs. The unit is now in a standby condition.

III. CALORIMETRY*

(W. N. Hubbard, H. M. Feder)

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

The basic data needed are heats of formation at 25 C. Part of the program of the group consists of determinations of heats of formation by 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 compounds of interest that are difficult to burn in oxygen, the techniques were modified so that fluorine could be used as the oxidant.

The accumulation of basic heat 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, values of heats of formation have been published for boron trifluoride, molybdenum hexafluoride, and the tetrafluorides of titanium, zirconium, hafnium, and silicon. The heats of combustion in fluorine of two compounds, boron nitride and silicon dioxide, have been determined by fluorine bomb calorimetry. To obtain the heat of formation for boron nitride required the use of the value obtained previously for boron trifluoride, while the value for silicon tetrafluoride was needed to obtain the heat of formation of silicon dioxide. Similarly, the heats of formation of boron trifluoride and zirconium tetrafluoride will be used in the current study of zirconium diboride.

A. Combustions of Zirconium Dihydride and Zirconium Dideuteride in Oxygen

(R. L. Nuttall, D. R. Fredrickson)

In a previous report (ANL-6477, page 156), results were presented for the heats of formation of zirconium dihydride and zirconium dideuteride, and the problem of oxygen contamination of the samples used was discussed. In the last quarterly report (ANL-6569, page 130), it was reported that measurements of the heat of combustion were being repeated with new samples of a lower oxygen content. The amount of oxygen in the new zirconium dihydride sample was 564 ppm; the new zirconium dideuteride sample contained 562 ppm oxygen.

The energies of combustion of these new samples of zirconium dihydride and zirconium dideuteride have been determined by means of a series of combustions in a platinum-lined bomb in the rotating bomb

*A summary of this section is given on pages 12 and 13.

calorimeter. The new values found were: for zirconium dihydride $\Delta E_{c298}^{\circ} = -290.03 \pm 0.24$ kcal/mole for the reaction

and for zirconium dideuteride $\Delta E_{c298}^{\circ} = -290.77 \pm 0.18$ kcal/mole for the reaction

Using these data and the heats of formation values of zirconium dioxide ($\Delta H_{f298}^{\circ} = -261.5 \pm 0.2$ kcal/mole), water ($\Delta H_{f298}^{\circ} = -68.3174$ kcal/mole), and deuterium oxide ($\Delta H_{f298}^{\circ} = -70.4133$ kcal/mole), the following enthalpy of formation values were calculated: $\Delta H_{f298}^{\circ} (\text{ZrH}_2) = -38.90 \pm 0.31$ kcal/mole for the reaction

and $\Delta H_{f298}^{\circ} (\text{ZrD}_2) = -40.25 \pm 0.27$ kcal/mole for the reaction

In each case the uncertainty reported is the standard deviation of the mean.

Figure 61

COMBUSTION BOMB WITH SAMPLE-SUPPORT ARRANGEMENT FOR OXYGEN COMBUSTION OF ZIRCONIUM DIHYDRIDE OR ZIRCONIUM DIDEUTERIDE

Figure 61 is a diagram showing the bomb and sample-support arrangement used for the combustions. The sample was contained in a sealed Mylar bag, which rested on a pressed zirconia disc in a platinum dish. The dish or crucible rested on a heavy platinum plate and was surrounded by a platinum shield. At the start of the experiment, the bomb also contained one ml of water in a platinum thimble and 15 atm of pure oxygen. Ignition of the cotton thread fuse was accomplished by heating the platinum ignition wire to red heat with a known amount of electrical energy. Under these conditions, the sample burned completely to zirconium dioxide and water or to zirconium dioxide and deuterium oxide.

The results of the combustion experiments for zirconium dihydride and zirconium dideuteride are presented in Tables 39 and 40. The entries in the tables are defined as follows: (1) m' , the amount of material burned corrected to the weight in vacuum; (2) Δt_c , the observed increase in the calorimeter temperature, corrected for heat exchange between the calorimeter and its surroundings; (3) ΔE_{IBP} , the total energy change in each combustion when carried out isothermally at 25 C; (4) ΔE other corrections, the net correction for ten minor corrections to the measured energy applied in such a manner that the resultant energy applies to a standard-state reaction; (5) ΔE Mylar, the energy associated with the combustion of the Mylar bag, based on a value of -5477.19 ± 1.03 cal/g Mylar (reported in ANL-6477, page 158); (6) ΔE cotton, the energy associated with the combustion of the cotton thread fuse, based on a value of 4050 cal/g cotton which was obtained in this laboratory; (7) $n' \Delta E_c$, the standard change in internal energy due to the combustion of m' grams of the sample according to Equations 1 or 2 (the sum of items 5 and 6 is subtracted from the sum of items 3 and 4 to give item 7); (8) $\Delta E_c^\circ/M$, the standard energy of combustion for one gram of sample; (9) mean $\Delta E_c^\circ/M$, the mean standard energy of combustion per gram of sample; (10) the energy correction per gram of sample for impurities in the sample; (11) $\Delta E_c^\circ/M$, the standard energy of combustion per gram for pure zirconium dihydride or zirconium dideuteride; and (12) ΔE_c° , the standard energy of combustion per mole of pure zirconium dihydride or zirconium dideuteride. Entries 9 to 12 list also the uncertainty expressed as the standard deviation of the mean.

Table 39

COMBUSTION OF ZIRCONIUM DIHYDRIDE IN OXYGEN

	Entries explained in text				
1. m' (g)	1.0878	1.0914	1.1004	1.0972	1.0935
2. Δt_c (C)	1.01495	1.01454	1.02613	1.02168	1.01841
3. ΔE_{IBP} (cal)	-3636.68	-3635.28	-3676.84	-3660.68	-3648.96
4. ΔE other corrections (cal)	-2.03	-2.11	-1.01	-0.70	-0.70
5. ΔE Mylar (cal)	-249.76	-247.02	-253.05	-256.33	-257.43
6. ΔE cotton (cal)	-5.75	-5.79	-5.67	-5.43	-5.67
7. $n' \Delta E_c$ (cpd)(cal)	-3383.20	-3384.58	-3419.13	-3399.62	-3386.56
8. $\Delta E_c^\circ/M$ (cal/g)	-3110.13	-3101.14	-3107.17	-3098.45	-3096.99
9. Mean $\Delta E_c^\circ/M$ for samples	$= -3102.77 \pm 2.53$ cal/g				
10. Energy correction for impurities	$= -7.77 \pm 0.67$ cal/g				
11. $\Delta E_c^\circ/M$ for pure ZrH_2	$= -3110.54 \pm 2.62$ cal/g				
12. ΔE_c° for pure ZrH_2	$= -290.03 \pm 0.24$ kcal/mole				

Table 40

COMBUSTION OF ZIRCONIUM DIDEUTERIDE IN OXYGEN

Entries explained in text

1. m' (g)	1.0839	1.1147	1.1058	1.1043
2. Δt_c (C)	0.99121	1.01975	1.00978	1.00910
3. ΔE_{IBP} (cal)	-3551.42	-3653.77	-3618.02	-3615.57
4. ΔE other corrections (cal)	-1.49	-0.71	-1.41	-2.35
5. ΔE Mylar (cal)	-245.38	-248.66	-248.66	-251.95
6. ΔE cotton (cal)	-5.87	-5.55	-5.75	-5.99
7. $n' \Delta E_c$ (cpd)(cal)	-3301.66	-3400.27	-3365.02	-3359.98
8. $\Delta E_c^\circ/M$ (cal/g)	-3046.09	-3050.39	-3043.06	-3042.63
9. Mean $\Delta E_c^\circ/M$ for sample =	-3045.54 ± 1.79 cal/g			
10. Energy correction for impurities =	-7.49 ± 0.66 cal/g			
11. $\Delta E_c^\circ/M$ for pure ZrD_2 =	-3053.03 ± 1.91 cal/g			
12. ΔE_c° for pure ZrD_2 =	-290.77 ± 0.18 kcal/mole			

A very important part of the study was the calculation of item 10, the combined correction for impurities in the sample. Because analytical results were the basis for the corrections, the following precautions were taken to ensure that the analytical samples of the two compounds were representative. (1) All combustion samples for a series of zirconium dihydride or zirconium dideuteride combustions were bagged on the same day; and (2) sampling for oxygen analysis was done in the dry box just prior to and during the course of the bagging operations.

The most significant impurity in each compound was oxygen, which was assumed to be combined as zirconium dioxide. The thermal correction for this impurity amounted to approximately 0.22 percent for both zirconium dihydride and zirconium dideuteride samples. The other impurities were magnesium, copper, iron, and lead, which were found by spectrochemical analysis, and nitrogen, carbon, and hydrogen (in the deuteride), which were found by chemical analysis. For calculation of the impurity correction, it was assumed that magnesium was present in the sample as MgO , that the other metals were present in their elemental state, and that nitrogen, carbon, and hydrogen were present as ZrN , ZrC , and ZrH_2 . The products of combustion of the impurities were assumed to be Cu_2O_3 , Fe_2O_3 , PbO_2 , ZrO_2 , N_2 , and CO_2 . Water and magnesium oxide were assumed to be unreactive. These impurities contribute a 0.03 percent correction to the energy evolved.

B. Combustions of Magnesium and Cadmium in Fluorine (E. Rudzitis and R. Terry)

Values of the enthalpies of formation for magnesium difluoride and cadmium difluoride which were obtained in a calorimetric study of combustions of magnesium and cadmium in fluorine were presented in the last quarterly report (ANL-6569, page 130). The series of experiments with magnesium consisted of five acceptable runs, which is a sufficient number of runs provided that satisfactory precision and certainty are obtained. However, in this series of experiments, the largest sample yielded the lowest heat of combustion per gram and the smallest sample yielded the highest result. Consequently, it was decided to carry out a few additional experiments to determine whether the result obtained was truly related to the mass of sample burned. The latter would be a strong indication of a systematic error in the measurements. In the course of making the additional runs, improved analytical data were obtained which could be applied to the earlier runs. Also, a more precise application of some of the thermal corrections was made to both sets of data. Revised data and new data for magnesium combustions in fluorine, which are presented below, do not indicate the possible systematic error mentioned above in the measurements.

1. Magnesium

The results of magnesium combustions in fluorine are presented in Table 41. The series consists of twelve acceptable runs.

Table 41
MAGNESIUM COMBUSTIONS IN FLUORINE
Entries explained in text

(1) Experiment No.	1	2	3	4	5	6	7	8	9	10	11	12
(2) m' (g)	0.29074	0.30037	0.29776	0.26984	0.30434	0.26424	0.19416	0.20720	0.37890	0.30386	0.24483	0.26257
(3) Δt_c (C)	0.88524	0.91244	0.90543	0.81376	0.91852	0.79429	0.58914	0.62672	1.14185	0.92565	0.74603	0.80350
(4) $\mathcal{E}$ calor Δt_c (cal)	-3189.6	-3287.6	-3262.4	-2932.1	-3309.5	-2861.9	-2114.6	-2249.5	-4098.4	-3322.4	-2677.7	-2884.0
(5) ΔE cont (cal)	-10.6	-10.5	-9.5	-8.1	-8.2	-6.9	-8.6	-5.5	-11.4	-7.1	-5.2	-5.5
(6) ΔE ign (cal)	0.1											
(7) ΔE gas (cal)	-0.5	-0.5	-0.5	-0.5	-0.6	-0.6	-0.5	-0.3	-0.5	-0.4	-0.3	-0.3
(8) ΔE imp (cal)	47.3	28.3	15.8	21.8	15.1	9.7	7.3	9.5	18.5	23.5	35.7	44.2
(9) $\Delta E_c^0 / M$ (cal/g)	-10846	-10887	-10937	-10817	-10853	-10824	-10900	-10838	-10799	-10881	-10813	-10837

Mean $\Delta E_c^0 / M$ for magnesium: $-10,852 \pm 12$ cal/g for 0.11 percent^a

^aStandard deviation of the mean.

The entries in the table are defined as follows: (1) experiment number; (2) m', the mass of sample burned; (3) Δt_c , the observed increase in calorimeter temperature, corrected for heat exchange between the calorimeter and its surroundings; (4) $\mathcal{E}$ calor Δt_c , the energy equivalent of the calorimeter multiplied by Δt_c ; (5) ΔE cont, the energy absorbed by the contents of the bomb; (6) ΔE ign, the electrical energy introduced to ignite

the sample; (7) ΔE_{gas} , the correction of the bomb gases to standard state conditions; (8) ΔE_{imp} , the energy evolved by fluorination of the oxide impurities in the sample and the support discs; (9) $\Delta E_{\text{C}}^{\circ}/M$, the sum of items 4 through 8 divided by the mass of metal burned represents the standard energy change per gram of sample at 25 C for the reaction

in which each reactant and product is in its standard state. Mean $\Delta E_{\text{C}}^{\circ}/M$ is the mean standard energy of combustion per gram of sample.

Some of the more important corrections were determined as follows. The mass of metal burned was obtained by subtracting the mass of the unburned metal and the mass of the impurities from the mass of the sample initially placed in the bomb. The weight correction for the impurities in the sample was made on the assumption that nitrogen, hydrogen, and carbon are adsorbed on the sample as nitrogen, water, and carbon dioxide, respectively, and that oxygen and fluorine (due to prefluorination) are bound as metal oxide and fluoride, respectively. The mass of the unburned metal was determined by treatment of the residue of the combustion with hydrochloric acid and gasometric measurement of the hydrogen evolved on the assumption that the amount of unburned metal was equivalent to the amount of hydrogen evolved.

The thermal corrections were based on the results of mass-spectrometric analysis of the combustion gases. The only gaseous component of significance was oxygen. It was assumed that the amount of metal oxide fluorinated was equivalent to the net amount of oxygen found in the combustion gases. Nitrogen and small amounts of carbon dioxide and water also present in the combustion gases were assumed to have originated from desorption from the sample and sample-support disc during the combustion process. No thermal corrections were made for the nitrogen, carbon dioxide, and water found. Small amounts of tetrafluoromethane and silicon tetrafluoride, probably originating from the fluorination of carbon dioxide and silicon dioxide, were also detected in the combustion gases. Uncertainties in the analysis and a self-compensating effect in the overall application of the oxygen correction did not warrant an application of specific thermal corrections for the small amounts of tetrafluoromethane and silicon tetrafluoride present. It is likely that a portion of the adsorbed water reacted with fluorine to form hydrogen fluoride and oxygen, although no hydrogen fluoride was detected in the combustion gases. No correction was made for this possible reaction. Again, the thermal effect is partially compensated in the application of the oxygen correction.

From the mean value obtained for $\Delta E_{\text{C}}^{\circ}/M$, $-10,852 \pm 12$ cal/g, the standard enthalpy of formation, ΔH_{298}° , of crystalline magnesium difluoride was calculated to be -264.4 ± 0.6 kcal/mole. The uncertainty

given is twice the "overall" standard deviation, in the calculation of which the standard deviation of the experimental results is so much greater than the standard deviation of other known uncertainties (e.g., the uncertainty in the calibration series, the accepted value for the heat of combustion of benzoic acid, and others) that it is substantially the sole contributing factor. The ΔH_{298}° value obtained in this study for magnesium difluoride is within the range of values (in kcal/mole) reported in the literature: -268.0 ± 1.8 was obtained by measuring the heat of the reaction, $\text{Mg} + \text{PbF}_2 = \text{MgF}_2 + \text{Pb}$;³⁰ -260.9 and -266.2 were derived from the heats of solution of magnesium³¹ and magnesium hydroxide³² in hydrofluoric acid; -260.2 was calculated from the temperature of hydrolysis equilibrium of magnesium difluoride.³³

2. Cadmium

Recently obtained analytical data and a re-evaluation of the thermal corrections for the study of the heat of formation of cadmium difluoride has led to revision of the data for cadmium reported in ANL-6569, page 131. The revised data are reported in Table 42. The definitions of the numbered items are identical with those for Table 41 except that item 9, $\Delta E_C^\circ/M$, refers to the standard energy of combustion per gram of sample at 25 C for the reaction

Table 42

CADMIUM COMBUSTIONS IN FLUORINE

Entries explained in text

(1) Experiment No.	1	2	3	4	5	6
(2) m ^l (g)	2.38612	2.01278	1.97651	1.72218	2.01204	1.95352
(3) Δt_c (C)	0.98829	0.82956	0.81358	0.71167	0.82871	0.80496
(4) $\mathcal{E}_{\text{calor}} \Delta t_c$ (cal)	-3560.9	-2988.9	-2931.4	-2564.2	-2985.9	-2900.3
(5) ΔE_{cont} (cal)	-7.5	-3.6	-3.3	-3.1	-3.6	-3.7
(6) ΔE_{ign} (cal)	$\longleftarrow \hspace{1.5cm} 0.1 \hspace{1.5cm} \longrightarrow$					
(7) ΔE_{gas} (cal)	-0.4	-0.4	-0.4	-0.3	-0.4	-0.4
(8) ΔE_{imp} (cal)	21.3	2.3	6.9	7.1	2.3	3.1
(9) $\Delta E_C^\circ/M$ (cal/g)	-1486.7	-1485.8	-1482.0	-1486.8	-1484.2	-1485.1

Mean $\Delta E_C^\circ/M$ for cadmium: -1485.2 ± 0.9 cal/g
(or 0.06 percent)^a

^aStandard deviation of the mean.

³⁰Gross, P., Hyman, C., and Levy, D. L., Trans. Faraday Soc., 50, 477 (1954).

³¹von Wartenberg, H., Z. anorg. chem., 249, 100 (1942).

³²Torgeson, D. R., and Sahama, T. G., J. Amer. Chem. Soc., 70, 2156 (1948).

³³Domange, L., Ann. chim., 7, 225 (1937).

From the data in the table, the standard enthalpy of formation, ΔH_{298}° , for cadmium difluoride is calculated to be -167.5 ± 0.2 kcal/mole. This value is higher than the values obtained from the literature: -165.2 and -161.6 kcal/mole. These values were derived from the temperature dependence of the gaseous equilibrium measurements on the systems $\text{CdF}_2\text{-H}_2$ ³⁴ and $\text{CdF}_2\text{-H}_2\text{O}$,³⁵ respectively. A value of -165.3 kcal/mole was calculated from the temperature dependence of emf measurements on the system, cadmium-amalgam, cadmium difluoride, hydrofluoric acid, lead fluoride, lead amalgam.³⁶ The original data³⁶ were corrected by means of an improved value for the potential of the lead-amalgam, lead fluoride electrode³⁷ and also improved data for the vapor pressure of aqueous hydrofluoric acid.³⁸ The results of our study yield for the standard Gibbs energy of formation, ΔG_{298}° (CdF_2), the value -155.5 kcal/mole, which is in close agreement with the corresponding value of -155.3 kcal/mole obtained from the emf measurements³⁶ as corrected.^{37,38}

C. Combustions of Aluminum and Zinc in Fluorine
(E. Rudzitis, R. Terry)

For combustions of aluminum and zinc in fluorine, the techniques developed for combustion of magnesium and cadmium in fluorine were found to be satisfactory with minor modifications. The calorimetric experiments with aluminum have been completed, and a preliminary series of combustions with zinc has been started.

For the aluminum combustions the sample was in the form of a mound of coarse prefluorinated filings supported on an aluminum fluoride disc, and covered by another disc to prevent spattering of the sample out of the combustion zone. The discs were made by cold pressing aluminum fluoride powder, presintering for a short period at 1000°C , and prefluorinating at 600°C . Ignition of the sample was accomplished by electrical energy with a short fine fuse wire. Use of aluminum for the fuse wire was found to be unsatisfactory, and in the final runs a cadmium fuse wire was used. Although the experimental work is substantially complete, calculation of a final value of the enthalpy of formation of aluminum fluoride is not complete. However, preliminary indications are that the result will be close to two values, -356.3 ³⁹ and -357.0 ⁴⁰ kcal/mole, determined by measurements of the heat of the reaction

³⁴Jellinek, K., and Rudat, A., *Z. anorg. Chem.*, **175**, 28 (1928).

³⁵Domange, L., *loc. cit.*

³⁶Jahn-Held, W., and Jellinek, K., *Z. Elektrochem.*, **42**, 401 (1936).

³⁷Broene, H. H., and deVries, T., *J. Amer. Chem. Soc.*, **69**, 1644 (1947).

³⁸Brosheer, J. C., Lenfesty, F. A., and Elmore, K. L., *Ind. Eng. Chem.*, **39**, 423 (1947).

³⁹Gross, P., Hayman, C., and Levi, D. L., *Trans. Faraday Soc.*, **53**, 1601 (1957).

⁴⁰Kolesov, V. P., Martinov, A. M., and Skuratov, S. M., *Bull. Chem. Thermodynamics*, **4**, 26 (1961).

and to a value recently determined by combustions of a mixture of aluminum and polytetrafluoroethylene in fluorine.⁴¹

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

Because of considerable interest in the thermochemistry of uranium compounds, part of the calorimetric program has been directed towards development of methods for their study. Some of the compounds may be studied by oxygen bomb calorimetry, for which the important auxiliary datum, $\Delta H_{298}^\circ (\text{U}_3\text{O}_8)$, is reasonably well known. Many of the compounds, however, will have to be studied by fluorine bomb calorimetry, for which the corresponding auxiliary datum, $\Delta H_{298}^\circ (\text{UF}_6)$, is not well known. From the most recent critical survey of thermochemical properties of uranium, one obtains for the "selected value" of the enthalpy of formation of uranium hexafluoride gas, $\Delta H_{298}^\circ (\text{UF}_6, \text{g}) = -511.5 \text{ kcal/mole}$ with an estimated uncertainty of $\pm 6 \text{ kcal/mole}$, or more than one percent. Thus there was a need for a redetermination of the enthalpy of formation of uranium hexafluoride.

Preliminary measurements of the enthalpy of formation of uranium hexafluoride gas were reported in ANL-6333, p. 124. The value $-509 \pm 3 \text{ kcal/mole}$ was calculated for $\Delta H_{298}^\circ (\text{UF}_6, \text{g})$ from the mean of three measurements. The uncertainties in the measurements were discussed, and it was shown that considerable improvement in experimental techniques and/or analytical procedures would have to be developed to reduce the uncertainties in the measurements. The development of combustion techniques to obtain more nearly complete combustions and analytical procedures to define the products of incomplete combustion has been discussed in ANL-6379, page 129; ANL-6413, page 102; ANL-6477, page 163; and ANL-6543, page 165.

During this reporting period, combustion and analytical techniques were sufficiently developed that calorimetric measurements were resumed. The most important developments were (1) a technique for burning about three times as much sample per combustion, which reduced to one-third its original effect the significance of the apparently constant amount of incompletely burned combustion products, and (2) techniques, discussed in the reports cited above, for better quantitative definition of the incompletely burned combustion products. Preliminary calculations of the results of four combustion runs indicate that the value that will be obtained for the enthalpy of formation of uranium hexafluoride gas will fall within the range of $-509 \pm 3 \text{ kcal/mole}$ reported earlier but will have an uncertainty approximately an order of magnitude smaller.

⁴¹Domalski, E. S., and Armstrong, G. T., The Heat of Formation of Aluminum Fluoride by Fluorine Bomb Calorimetry, 17th Annual Calor. Conf., U. of California (1962).

E. Combustions of Zirconium Diboride in Fluorine
(G. K. Johnson* and E. Greenberg)

It was pointed out in a previous report (ANL-6543, page 164) that: (1) the values of the heat of formation of zirconium diboride that can be estimated from currently available data vary over a range of more than 30 kcal; (2) the heats of formation of zirconium tetrafluoride⁴³ and boron trifluoride⁴⁴ have already been determined in this laboratory and, consequently, we are in a uniquely favorable position to study zirconium diboride by fluorine bomb calorimetry; and (3) a high-purity sample of zirconium diboride has been made available to this laboratory through the "Thermodynamic and Kinetic Studies for a Refractory Materials Program" of the Wright Air Development Division.

During this reporting period, the preliminary exploratory work for the study has been completed and calorimetric measurements have been started. Work was performed on three principal problems: the development of an adequate combustion technique, the establishment of a suitable material for sample support, and the establishment of a suitable method for the determination of the amount of unburned zirconium diboride in the residue of the combustion.

It was found that the zirconium diboride sample, which arrived as small 20-g ingots from a zone-melting purification apparatus, did not ignite spontaneously in massive form. This led to experimentation with the combustion of the sample in the form of a rod. Although the combustions were satisfactory with this technique, the extreme hardness and brittleness of zirconium diboride caused severe difficulties in the fabrication of suitable sample rods. The fabrication of rods also resulted in an extravagant waste of sample.

When the sample was fractured to 200 to 300 mesh powder, it sometimes ignited spontaneously upon exposure to fluorine. The combustion technique finally established involved the combustion of zirconium diboride powder in a reaction vessel for hypergolic reactions⁴⁵ developed earlier in this Laboratory. This combustion bomb keeps the fluorine oxidant separate from the sample until reaction is desired. To insure reproducibly spontaneous ignition of the sample, approximately 50 mg of powdered sulfur was used as kindler under the zirconium diboride.

*Resident Student Associate from the University of Wisconsin.

⁴³Greenberg, E., Settle, J. L., Feder, H. M., and Hubbard, W. N., J. Phys. Chem., 65, 1168 (1961)

⁴⁴Wise, S. S., Margrave, J. L., Feder, H. M., and Hubbard, W. N., J. Phys. Chem., 65, 2157 (1961).

⁴⁵Nuttall, R. L., Wise, S., and Hubbard, W. N., Rev. Sci. Inst., 32, 1402 (1961). See also ANL-6287, page 126.

Of the many support materials tested in trial combustions (silica, sapphire, alumina, zirconia, zirconium tetrafluoride, aluminum trifluoride, zirconium, and nickel, all in the form of plaques or discs), only massive discs of zirconium and nickel were found to withstand the heat of the reaction. In both of these cases excessive deterioration of the support material was prevented by the formation of a protective fluoride coating. Of these two materials, zirconium proved the better choice, both because it introduced no extraneous material into the bomb and because the enthalpy of formation of zirconium tetrafluoride is known more accurately than that of nickel fluoride. After conditioning by several trial combustions, it was found that the zirconium disc lost, reproducibly, 2 to 3 mg in weight per combustion. A thermal correction could be easily and reliably made for this.

With the best technique developed, there remained approximately 2 to 3 mg of unburned zirconium diboride after a combustion. This was caused by a "cake" of zirconium tetrafluoride forming on the support and quenching the reaction. The amount of unburned zirconium diboride had to be determined to define the amount of reaction that occurred in the combustion. Attempts to separate the tetrafluoride and diboride physically proved unsuccessful. Chemical separations by dissolution were hindered due to the insolubility of some of the components of the mixture. Most colorimetric analyses for boron proved of little value due to interference of the fluoride ion.

A colorimetric analysis for boron was adopted which follows the method of Ross, Meyer, and White⁴⁶ for the analysis of boron in the presence of fluorides. The method involves a potassium carbonate fusion of the sample, dissolution in aluminum chloride-hydrochloric acid solution, an ether extraction of the boron, and the formation of a color by use of carminic acid. Preliminary data indicate that there is very little fluoride interference and that the method gives reproducible results.

F. Combustion of Niobium and Tantalum in Fluorine (E. Greenberg)

Preliminary exploratory combustion experiments have been carried out for combustions of niobium and tantalum in fluorine. The development of satisfactory combustion techniques for niobium and tantalum was reported in ANL-6333, page 127. In ANL-6569, page 232, it was reported that calorimetric studies awaited the procurement and analysis of high-purity samples. The niobium and tantalum samples have now been received and are currently being analyzed. Initial results indicate that the samples are satisfactory for calorimetric combustions. It is expected that the remaining analytical work will be completed shortly.

⁴⁶Ross, W. J., Meyer, A. S., Jr., and White, J. C., *Anal. Chem.*, 29, 810 (1957).

IV. REACTOR SAFETY*

The oxidation, ignition, and combustion of uranium and low-level binary uranium alloys are being studied to provide information which will help to minimize the hazards associated with handling these materials.

An experimental program to determine the rates of reaction of molten reactor fuel and cladding metals with water is continuing. Methods currently being used to examine these reactions are the condenser-discharge and volumetric methods in the laboratory and in-pile reactor transients in the TREAT reactor.

A. Metal-oxidation and Ignition Kinetics (L. Baker)

1. Theory of Uranium Ignition (L. Baker, J. G. Schnizlein, J. D. Bingle, A. J. Buhl**)

Studies of the isothermal oxidation of uranium at temperatures above 300 C were reported in previous quarterly reports (ANL-6413, page 160 and ANL-6543, page 168). The purpose of these studies was to provide reaction rate data needed to develop a better understanding of previously reported ignition data. A simple relationship between isothermal oxidation rates and ignition temperature should exist if the ignitions are purely thermal in character. A thermal ignition occurs by the accumulation of heat (i.e., the reacting system generates more heat than can be dissipated by heat loss mechanisms, leading to a rapidly increasing temperature).

Calculations were presented in the previous quarterly (ANL-6569, page 136) in which the rate laws found from isothermal studies of uranium oxidation were combined with a simple model of heat transfer. For unalloyed uranium samples having specific areas of 0.5 and 5 sq cm/g, computed ignition behavior was found to agree well with results of experimental burning curve ignition experiments.

It is evident from the computations that the unusual transition in uranium samples from an accelerating reaction to a decelerating reaction at 450 C plays an important role in the ignition process. It is also clear from previous studies that alloying additions to the uranium have profound effects on the transition. It was shown in a previous quarterly report (ANL-6543, page 174) that the presence of 1 atom percent aluminum in uranium prevents the transition entirely, whereas in the presence of 1 atom percent copper the oxide film formed after the transition is more protective than that formed on unalloyed uranium. Since the effect of aluminum in

*A summary of this section is given on pages 13 to 15.

**Summer employee from Oberlin College.

preventing the transition seems particularly important, studies of the isothermal oxidation of low-level aluminum-uranium alloys were continued. Results of previous studies of the ignition of uranium alloys by the burning curve method have been evaluated. In addition, ignition studies with a number of new uranium alloys were undertaken.

a. Isothermal Oxidation and Ignition of Low-level Aluminum-Uranium Alloys

Isothermal oxidation rates of a series of aluminum-uranium alloys were determined at 500 C in the stainless steel "heat sink" apparatus (see ANL-6543, page 168, for apparatus description). Oxidation curves are presented in Figure 62, and the reaction rates (slopes) after consumption of 10,000 μg of oxygen per square centimeter of surface are tabulated in Table 43. The results show that the oxidation rate increases regularly with increasing aluminum content. It is also clear from Figure 62 that the decelerating rates characteristic of unalloyed uranium at

Figure 62

ISOTHERMAL OXIDATION OF LOW-LEVEL
ALUMINUM-URANIUM ALLOYS AT 500 C
IN OXYGEN

Runs were made with nominal 1-cm cubes in the constant-volume pressure-pickup apparatus, ANL-6543, page 168, with an initial oxygen pressure of 500 mm and a final pressure of 100 mm. The alloys were prepared from BMI base metal.

the temperatures used gradually approach the accelerating rates reported for the 1130 ppm (1 a/o) alloy as the aluminum content is increased. The results also indicate that small differences in aluminum content are very likely the cause of the marked differences in the oxidation rates of uranium prepared at ANL (analyzed 15 ppm Al) and uranium prepared at BMI (analyzed 34 ppm Al).^{*} An important inference to be drawn from the data is that the transition to a protective oxide is progressively inhibited by increasing quantities of aluminum.

Table 43

COMPARISON OF OXIDATION RATES AT 500 C AND IGNITION
TEMPERATURES FOR SELECTED LOW-LEVEL
ALUMINUM ALLOYS OF URANIUM

Metal ^a	Ignition Temperature ^b (C)	Oxidation Rate, $\mu\text{g}/(\text{sq cm})(\text{min})$ at 500 C after 10,000 $\mu\text{g O}_2/\text{sq cm}$ Total Oxidation
ANL Base Metal (15 ppm Al)	595	915
BMI Base Metal (34 ppm Al)	575	1,510
55 ppm Al	575	2,120
70 ppm Al	575	-
75 ppm Al	420	2,790
235 ppm Al	385	3,060
580 ppm Al	365	8,100
1,130 ppm Al (1 a/o)	355	19,800

^a The aluminum-uranium alloys were prepared from BMI base metal.

^b Determined by the burning curve technique in flowing oxygen for 8.5-mm cubes.

Values of the burning curve ignition temperature for the low-level aluminum-uranium 8.5-mm cubes are included in Table 43. In a burning curve experiment, samples are heated uniformly (usually at the rate of 10 C/min) in a flowing oxidizing atmosphere. The sample eventually begins to self-heat rapidly and ignite. The ignition temperature is obtained graphically from the temperature-time record.

The ignition temperatures given in Table 43 drop rather suddenly at an aluminum content^{**} of about 75 ppm, in contrast with the

^{*} A metallurgical difference also exists between the two metals: The ANL base metal is air-quenched, while the BMI base metal is as-cast. Detailed analyses of these metals may be found in ANL-5974, page 146.

^{**} The aluminum content was determined by chemical analysis and is subject to as much as a 15 percent error.

rather uniform increase of oxidation rate at 500 C. Evidently, at the 75-ppm level the transition to a protective oxide film on the samples is just sufficiently inhibited at 450 C so that heat generated by the reaction exceeds heat losses at all higher temperatures and ignition can occur. For the base metals and the 55- and 70-ppm alloys, which apparently undergo the transition to a protective oxide, the temperature must reach nearly 600 C before ignition can occur.

The shapes of the experimental burning curves, given in Figure 63, also show the presence of the transition region. The BMI base metal (34 ppm Al) and the 55- and 70-ppm alloys initially show a tendency to ignite at temperatures below 450 C. As protective oxide is formed following the transition, however, the temperature decreases to nearly the value of the furnace temperature.

Figure 63

BURNING CURVES IN OXYGEN FOR URANIUM-ALUMINUM ALLOYS

(8.5-mm cubes)

Alloys were prepared from
BMI base metal.

b. Ignition Studies of Other Uranium Alloys by the Burning Curve Method

Recent isothermal oxidation studies have added to the understanding of burning curve ignition experiments with unalloyed uranium and with low-level aluminum-uranium alloys. It is now pertinent to re-examine the effects of other additives to uranium. Burning curve ignition experiments of 34 different binary uranium alloys were reported

in ANL-5974, page 15. Results of studies with low-level aluminum and silicon alloys were reported in ANL-6145, page 140. Some 30 additional uranium alloys obtained from the Battelle Memorial Institute have now been studied.

The temperature-time plots for these 70 binary alloys are varied and complex, but reproducible. Examination of the plots revealed that two major factors are operating to alter the shape of the unalloyed uranium burning curves;* these effects may occur singly or in combination. One of the postulated effects has already been discussed in connection with aluminum alloys. It was shown that aluminum additions inhibit the transition to a protective oxide at 450 C. Other alloying agents that result in a rapid self-heating from below 450 C might also be assumed to inhibit the transition or delay it until higher temperatures are reached. Burning curves obtained with three bismuth alloys (see Figure 64), for example, show a rapid self-heating similar to that of the aluminum alloys shown at the left of Figure 63.

Figure 64
BURNING CURVES IN OXYGEN FOR
URANIUM-BISMUTH ALLOYS
(8.5-mm cubes)

provides a thermal halt, during which time protective oxide is built up. For some alloys, such as the 1-a/o copper alloy shown in Figure 66, the temperature remains at the temperature of the beta-gamma transition for some time.

The second effect postulated to be important in the understanding of uranium alloy ignitions is the tendency of certain alloying agents to render the high-temperature oxide more protective. This effect was shown by isothermal oxidation studies with copper. An isothermal oxidation curve for copper at 625 C is compared to those for the two base metals in Figure 65. Increased protectiveness in the post-transition temperature region with increased copper content is also shown in burning curves (see Figure 66). It is concluded from the curves in Figure 66 that the beta-gamma transition, generally recorded on burning curves at about 700 C,

* Burning curves for unalloyed uranium are given on the right-hand side of Figure 63.

Figure 65

ISOTHERMAL OXIDATION OF URANIUM AND 1 a/o COPPER-URANIUM ALLOY AT 625 C IN OXYGEN

Runs were made with nominal 1-cm cubes in the constant-volume pressure-pickup apparatus, (see ANL-6543, page 168), with an initial oxygen pressure of 500 mm and a final pressure of 100 mm. The 1-a/o copper alloy was prepared from BMI base metal.

Figure 66

BURNING CURVES IN OXYGEN FOR URANIUM-COPPER ALLOYS

(8.5-mm cubes)

Alloys were prepared from BMI base metal.

Curves for the 0.17- and 0.90-a/o bismuth alloys (see Figure 64) illustrate the case in which both of the effects described above are operative. The transition to a protective oxide was delayed until well above 450 C. The oxide produced following transition was very protective in the case of the 0.90 percent bismuth alloy, and the temperature did not rise significantly above the beta-gamma transition temperature for over 30 min. For the 0.17-a/o bismuth alloy, the effect was less marked, and thermocycling between the beta-gamma transition temperature and a

slightly higher temperature continued until the furnace temperature rose sufficiently to permit ignition. Thermocycling in the gamma phase was noted for many of the alloys studied.

Ignition temperatures obtained from the burning curves for all of the alloys studied are plotted in Figure 67.

Figure 67

THE EFFECT OF ALLOY ADDITIVES ON
THE BURNING CURVE IGNITION
TEMPERATURE OF 8.5-mm
URANIUM CUBES IN FLOWING OXYGEN

The following tabulation summarizes effects noted from the shapes of the individual burning curves:

Aluminum: The transition to protective oxide at 450 C was inhibited by aluminum concentrations above about 70 ppm (see Figure 63).

Beryllium: The transition to protective oxide at 450 C was inhibited at 0.37- and 1.08-a/o beryllium levels. However, the 0.66-a/o beryllium content had no effect, as compared with unalloyed uranium.

Bismuth: The transition to protective oxide at 450 C was inhibited for 0.17-, 0.39-, and 0.90-a/o bismuth alloys. Enhanced post-transition protectiveness was noted for 0.17- and 0.90-a/o alloys, particularly the latter. Some gamma-phase thermocycling was observed (see Figure 64).

Carbon: The transition to protective oxide was inhibited slightly in the range from 0.62 to 1.67 a/o carbon. Only at 1.06 a/o carbon did the transition to a protective oxide materially delay ignition as for pure uranium.

Cerium: The burning curve of the 400-ppm cerium alloy is very similar to that for ANL uranium (shown in Figure 63).

Chromium: The 0.86-a/o chromium alloy has a burning curve quite similar to that of 70-ppm aluminum (see Figure 63). This chromium alloy may be on the borderline with respect to inhibiting the transition to a protective oxide at 450 C.

Copper: In the post-transition temperature region, protectiveness of the oxide increased as the amount of copper in the alloy was increased (see Figure 66).

Hydrogen: There was no effect on the burning curve at the 0.35-a/o hydrogen level as compared with unalloyed uranium.

Iron: There was essentially no effect on the burning curve up to 2.1 a/o iron, as compared with unalloyed uranium.

Lead: The transition to protective oxide at 450 C was inhibited in the range from 0.23 to 0.62 a/o lead. There was enhanced post-transition protectiveness with thermocycling in the gamma phase at the three concentrations studied.

Molybdenum: The transition to protective oxide at 450 C was inhibited at 0.5-, 1.0-, and 2.0-a/o molybdenum levels. Enhanced post-transition protectiveness was noted in the 2-a/o alloy.

Nickel: There was no effect on the burning curve at the 1.0-a/o nickel level, as compared with unalloyed uranium.

Niobium: The transition to protective oxide at 450 C was inhibited in the range from 0.5 to 1.9 a/o niobium.

Palladium: The transition to protective oxide at 450 C was inhibited for the 1.1-a/o palladium alloy, following which enhanced post-transition protectiveness and thermocycling in the gamma phase were noted.

Platinum: The transition to protective oxide at 450 C was inhibited in the range from 0.6 to 2.1 a/o platinum. Enhanced post-transition protectiveness and thermocycling in the gamma phase were noted at the 0.6- and 1.1-a/o concentrations.

Rhodium: There was essentially no effect on the burning curves at the 1.2-a/o rhodium level as compared with unalloyed uranium.

Ruthenium: The transition to protective oxide at 450 C was inhibited for 0.5, 1.0, and 2.0 a/o ruthenium alloys. Enhanced post-transition protectiveness was noted in the 0.5- and 1.0-a/o concentrations, along with thermocycling in the gamma phase.

Silicon: Effects very similar to those of aluminum, with the transition to a protective oxide at 450 C inhibited at silicon concentrations from about 70 ppm up to 2.5 a/o. A 4.1-a/o silicon alloy showed no effect on the burning curve, however, as compared with unalloyed uranium.

Silver: There was no effect on the burning curve at the 0.22-a/o silver level as compared with unalloyed uranium.

Tantalum: The transition to protective oxide at 450 C was inhibited somewhat at 0.8 a/o tantalum. There was a very minor effect at 2.5 a/o tantalum.

Titanium: The transition to protective oxide at 450 C was inhibited in the range of 0.5 to 1.4 a/o for titanium.

Thorium: There was essentially no effect on the burning curve at the 1.2-a/o thorium level as compared with unalloyed uranium.

Vanadium: The transition to the protective oxide at 450 C was inhibited for the 0.7- to 1.1-a/o vanadium alloys, with enhanced post-transition protectiveness and some gamma-phase thermocycling noted. The 0.2-a/o vanadium alloy has a burning curve similar to that of the 70-ppm aluminum alloy (see Figure 63) and thus may be on the borderline with respect to inhibiting the transition to a protective oxide at 450 C.

Zirconium: There was no effect on the burning curve for 0.5 a/o zirconium, but the 1.0-a/o zirconium alloy inhibited the transition to protective oxide at 450 C slightly, and the 1.9-a/o zirconium alloy inhibited the transition even more so.

2. Burning Propagation and Ignition Studies - The Effect of Halogenated Hydrocarbons
(L. Leibowitz, L. W. Mishler)

It has been found that both the burning propagation velocity and the maximum burning temperature are lowered by the presence in air of a few percent of any one of a number of halogenated hydrocarbons (see ANL-6379, page 195, and ANL-6413, page 162). Because interest has been generated in the fire- and explosion-prevention properties of dibromotetrafluoroethane (Freon 114B2), measurements were carried out on the effect of this compound on the combustion of uranium and zirconium foil strips. Burning propagation velocities,* maximum burning temperatures, and ignition temperatures were measured in air containing two and four percent Freon 114B2. The values obtained are listed in Table 44, as well as previously reported results for certain other halogenated hydrocarbons (see ANL-6413, page 167).

Table 44

EFFECT OF VARIOUS GAS CONTAMINANTS ON BURNING
OF URANIUM AND ZIRCONIUM FOILS IN AIR

<u>Contaminant</u>	<u>2 Volume Percent of Contaminant</u>			<u>4 Volume Percent of Contaminant</u>	
	<u>Burning Curve</u> <u>Ignition Temp (C)</u>	<u>v^a</u>	<u>T^b</u>	<u>v^a</u>	<u>T^b</u>
I. <u>Uranium (foil, 0.013 x 0.3 cm)</u>					
None	380	0.52	1375	0.52	1375
CF ₂ Br-CF ₂ Br	320	0.36	1110	0.24	1025
CH ₃ CHF ₂	350	c		c	
CF ₃ Br	285	0.39	1205	0.38	1150
CH ₂ BrCl	320	0.39	1210	0.31	1150
II. <u>Zirconium (foil, 0.002 x 0.3 cm)</u>					
None	-	2.20	1595	2.20	1595
CF ₂ Br-CF ₂ Br	-	c		c	
CH ₃ CHF ₂	-	1.47	1235	1.40	1265
CF ₃ Br	-	c		c	
CH ₂ BrCl	-	1.61	1425	c	

^a Burning propagation velocity, cm/sec.

^b Maximum burning temperature, C.

^c Propagation did not occur.

* The rate of advance of a combustion zone along a wire or metal strip.

For reducing the burning propagation velocity of uranium foil, Freon 114B2 seems to be one of the best of the compounds tested, though not as effective as CH_3CHF_2 . Unlike CH_3CHF_2 , however, this substance does not form flammable mixtures with air. The burning curve ignition temperature of uranium foil was depressed 60 degrees by two volume percent Freon 114B2, however.

In tests with zirconium foil strips, Freon 114B2 prevented propagation, as had a number of other compounds tested earlier. The newly tested agent seems fairly attractive as a fire-protection compound.

3. Ignition of Irradiated Uranium (J. G. Schnizlein)

An important aspect of the ignition of uranium is the effect of irradiation on ignition behavior. Incidents reported in the literature (Chalk River, Canada,⁴⁷ and Windscale, England,⁴⁸ as well as several ignitions at Hanford⁴⁹) have been interpreted as indicating a greater pyrophoricity of uranium after irradiation. Therefore, studies of the ignition of irradiated uranium have been initiated.

It is certain that the release of fission products in the event of ignition of irradiated uranium constitutes a severe hazard. The release of fission products has been studied by Parker et al.,⁵⁰ Hilliard,⁵¹ Scott,⁵² and Megan et al.⁵³ at elevated temperatures. Some of these authors indicate a somewhat greater oxidation rate of irradiated uranium than of unirradiated metal, but there were uncertainties as to surface area and extent of irradiation. Hilliard⁵⁴ states that he noted increased oxidation rates in air only when uranium was irradiated above 10^{20} nvt (10^{-2} a/o burnup), at which point fission gas bubbles cause disruption of the oxide and increased surface area.

Zima concludes that, "The effect of irradiation on the pyrophoricity of uranium remains obscure. The evidence presented in this review does not indicate a strong irradiation influence. It is submitted that the two main effects of irradiation with respect to fuel element fires are: increase

⁴⁷ Greenwood, J. W., Contamination of the NRU Reactor in May 1958, AECL-850 (CRR-836) (May 1959).

⁴⁸ Accident at Windscale No. 1 Pile on Oct. 10, 1957, Her Majesty's Stationery Office, London (Nov 1957).

⁴⁹ Zima, G. E., Pyrophoricity of Uranium in Reactor Environments, HW-62442 (Jan 1960).

⁵⁰ Parker, G. W., Creek, G. E., Martin, W. J., and Barton, C. J., Fuel Element Catastrophe Studies: Hazards of Fission Product Release from Irradiated Uranium, ORNL-CF-60-6-24 (June 1960).

⁵¹ Hilliard, R. K., Fission Product Release from Uranium Heated in Air, HW-60689 (Aug 1959).

⁵² Scott, A. J., Fission Product Release by High Temperature Uranium Steam Reaction, HW-62604 (Nov 1959).

⁵³ Megan, W. J., Chadwick, R. C., Wells, A. C., and Bridges, J. E., *J. Nuclear Science*, 15, 176 (1961).

⁵⁴ Hilliard, R. K., Fission Product Release from Uranium-Effect of Irradiation Level, HW-72321 (June 1962).

in the potential active surface associated with a given mass of U through the development of cracks, and porosity; self heating from radioactive decay." There have been numerous studies on the effect of irradiation on the mechanical properties of uranium. Directional growth, surface roughening, and swelling are commonly observed. Chellew (see ANL-6379, page 37), Kittel, and others at Argonne National Laboratory have reported that when highly irradiated uranium is heated to approximately 650 C, the sample swells and becomes somewhat porous. This post-irradiation swelling would very likely result in ignition if it occurred in the presence of air. LaPlante (see ANL-6569, page 31) has observed a strongly exothermic reaction with nitrogen at the same approximate temperature.

It has been decided to enclose the uranium samples in a constraintment jacket in an effort to avoid the complications of surface roughening, directional growth, and swelling during irradiation. Conditions are to be chosen to maintain a low sample temperature (less than 300 C) during irradiation. In addition, the sample size (0.25 x 0.20-in.-dia pins) is to be such that its ignition temperature, before irradiation, would be approximately 550 C. It is hoped that thereby the complication of "post-irradiation swelling" may be avoided.

Enriched uranium pins are to be used so that adequate burnup can be obtained in a reasonable time. These pins have been requested from Metallurgy Division, and the constraintment jackets are being fabricated by the shops. Possibly, irradiations will start in the fourth quarter of 1962.

B. Metal-Water Reactions (L. Baker)

1. Condenser-discharge Method (L. Baker, R. Warchal, R. Koonz)

The condenser-discharge experiment is an attempt to obtain fundamental rate data under experimental conditions similar to those encountered during a serious accident in a nuclear reactor. Either a nuclear runaway or a sudden loss of coolant during operation of a water-cooled reactor could result in contact of very hot fuel and cladding metals with water or steam and might involve fine particles. The condenser-discharge experiment simulates the limiting case of a nuclear incident in that the heating time is very short and very fine metal particles are produced.

In the condenser-discharge experiment, metal wires are rapidly melted and dispersed in a water-filled cell by a surge current from a bank of condensers. The energy input to the wire is used to calculate the initial reaction temperature. The transient pressure measures the reaction rate, the amount of hydrogen generated gives the extent of reaction, and the particle size of residue indicates the surface area exposed to reaction.

Analysis of results is based on one of the usual laws of metal oxidation (such as the parabolic rate law) and on the laws of gaseous diffusion and heat transfer. In this way, an attempt is made to interpret experimental work as it proceeds.

The results of a series of runs with stainless steel-316 wires in room-temperature water was reported in a previous quarterly report (ANL-6543, page 182). Similar series of runs with stainless steel-316 wires in nominal 100 C and 200 C water have now been completed. In addition, particle size measurements for the stainless steel runs have been completed. Complete results of studies with 30- and 60-mil stainless steel-316 wires are presented in Table 45 and Figure 68. The runs were made in the high-pressure reaction cell described in ANL-6231, page 156.

Table 45

STAINLESS STEEL-316 WATER REACTION DATA FROM HIGH-PRESSURE CONDENSER DISCHARGE APPARATUS

Run	Calc Initial Metal Temp (C) and Physical State	Ambient Water Temp (C)	Percent Reaction ^a	Sauter Mean Particle Diameter (μ)	Appearance of Residue	Run	Calc Initial Metal Temp (C) and Physical State	Ambient Water Temp (C)	Percent Reaction ^a	Sauter Mean Particle Diameter (μ)	Appearance of Residue
Runs in Room-temperature Water 30 mil Wires						Runs in Nominal 100 C Water 30-mil Wires					
303	1370 solid	25	0.0	1150 ^b	Distorted	332	2200 liquid	105	12.2	290	Fine Particles
304	1370 10% liquid	25	0.0	1150 ^b	Large Particles	336	2200 liquid	104	11.1	290	Fine Particles
182	1370 100% liquid	25	4.7	250	Fine Particles	334	2500 liquid	115	15.8	300	Fine Particles
184	1400 liquid	25	2.6	430	Fine Particles	263	2700 liquid	110	24.6	320	Fine Particles
302	1400 liquid	25	2.7	250	Fine Particles	330	2900 liquid	107	22.0	180	Fine Particles
181	1400 liquid	25	4.7	310	Fine Particles	266	3100 liquid	105	24.5	220	Fine Particles
198	1400 liquid	25	3.1	520	Fine Particles	328	3700 liquid	102	32.2	100	Powder
180	1500 liquid	25	4.0	320	Fine Particles	312	-- part vapor ^c	107	54.1	-	Powder
183	1500 liquid	25	4.9	380	Fine Particles	Runs in Nominal 100 C Water 60-mil Wires					
185	1600 liquid	25	6.3	310	Fine Particles	327	1370 80% liquid	113	2.0	-	Jagged Pieces
308	2100 liquid	25	6.4	220	Fine Particles	323	1600 liquid	120	4.3	-	Jagged Pieces
316	2300 liquid	25	5.4	630	Fine Particles	Runs in Nominal 200 C Water 30 mil Wires					
315	2300 liquid	25	4.5	320	Fine Particles	333	2300 liquid	200	12.9	480	Fine Particles
264	2500 liquid	25	11.6	170	Fine Particles	335	2700 liquid	209	18.5	380	Fine Particles
265	3100 liquid	25	17.5	230	Fine Particles	331	3000 liquid	196	25.8	240	Fine Particles
314	3800 liquid	25	35.9	130	Powder	329	3700 liquid	193	35.8	260	Fine Particles
Runs in Room-temperature Water 60-mil Wires						Runs in Nominal 200 C Water 60 mil Wires					
319	1000 solid	25	0.2	2280 ^b	Distorted	325	1000 solid	206	0.5	2280 ^b	Intact (blackened)
311	1200 solid	25	0.1	2280 ^b	Bent and Cracked	187	1100 solid	178	0.7	2280 ^b	Intact (blackened)
317	1370 50% liquid	25	0.6	1100	Large Particles	326	1500 liquid	200	3.4	-	Jagged Pieces
318	1370 90% liquid	25	1.6	920	Fine Particles	324	1800 liquid	176	7.8	-	Jagged Pieces
322	1400 liquid	25	1.8	900	Fine Particles						
321	1600 liquid	25	3.0	980	Fine Particles						

^aBased on reaction to Cr₂O₃, NiO, and FeO

^bSize of spheres that would have the same surface to volume ratio as the original wire

^cEnergy input was 1043 cal/g

Figure 68
STAINLESS STEEL (316)-WATER REACTION
BY THE CONDENSER-DISCHARGE METHOD

Some runs in heated water were performed in pairs in which the only variable was the water temperature: one run in water at 100 C (15 psia) and the other in water at 200 C (225 psia). No significant difference in percent of metal reacted was noted between runs in water at 100 C and 200 C. As a group, the runs in which water was heated to 100 or 200 C gave significantly more metal-water reaction than the runs in room-temperature water. A similar finding was reported for zirconium (see ANL-6333, page 212) and for uranium (see ANL-6413, page 174). For the stainless steel reaction, however, the difference between results in heated water and in room-temperature water was smaller than was observed for zirconium and uranium. For stainless steel runs, the total extent of reaction at high initial temperatures of the metal (e.g., 36 percent reaction at an initial metal temperature of 3700 C) also was smaller than with zirconium or uranium under similar conditions (see ANL-6477, page 188; ANL-6413, page 174). These two findings indicate that the reaction rate is controlled predominantly by a chemical rate law, even at very high temperatures. Gaseous diffusion of water vapor through the evolving hydrogen, shown to be of major importance in the zirconium-water reaction, appears to be less important in the stainless steel-water reaction.

A mathematical analysis of the results of studies of the zirconium-water reaction was recently published as a topical report (ANL-6548, May 1962). Computations were made with an analog computer. It was concluded in this study that a more reliable analysis is obtained

with data from isothermal rate studies at lower temperatures (for example, up to 1800 C). Isothermal studies with uranium were reported in the previous quarterly report, (ANL-6569, page 148). Similar isothermal studies with stainless steel are planned.

The equations used in the analog computer study have now been programmed on the IBM-704 digital computer to aid in the analysis of uranium-water reaction obtained by condenser-discharge experiments. Similar analysis of the stainless steel-water reaction will be undertaken as isothermal rate data become available,

2. Isothermal Studies of the Reaction of Steam with Low-level Aluminum-Uranium Alloys by the Volumetric Method
(R. E. Wilson, R. Koonz)

A knowledge of the rates of reaction of metals with steam under isothermal conditions is necessary for the prediction of metal-water reactions under the conditions of a reactor accident. A volumetric experiment was designed to study metal-steam reactions; the volume of hydrogen evolved was used as a continuous measure of the extent of reaction. The uranium sample (one-cm cube) was supported on a stainless steel-clad thermocouple, centered in the sample volume. Samples were heated by induction to the test temperature in flowing steam at one atmosphere pressure. After passing the sample, the steam was condensed and the hydrogen produced by metal-water reaction was collected and measured. A more detailed description of the apparatus and the procedure is given in ANL-6543, page 185.

Results of studies of the uranium-steam reaction between 400 and 1200 C were reported in the previous quarterly (ANL-6569, page 148). The reaction was found to be linear at 400 C, and parabolic at 500 C and above. The linear-parabolic transition temperature, however, was reported by Hopkinson⁵⁵ to be 880 C.

It is known from studies of the uranium-oxygen reaction that small quantities of aluminum alloyed with the uranium have a profound effect on the reaction at temperatures in the vicinity of 500 C (see page 176 of this report). In that study it was observed that for the reaction of uranium with oxygen (see ANL-6543, page 175), alloying additions of aluminum prevented a transition from an accelerating reaction below 450 C to a decelerating reaction above 450 C. It was decided, therefore, to study the reaction of low-level aluminum-uranium alloys with steam to determine if a similar effect occurs in the steam reaction.

⁵⁵ Hopkinson, B. E., J. Electrochem. Soc., 106, 102 (1959).

Typical runs with uranium containing 1 a/o aluminum are plotted in Figure 69. The reaction at 400 C is approximately linear, whereas

Figure 69

HYDROGEN EVOLUTION FROM URANIUM-
1 a/o ALUMINUM ALLOY IN STEAM -
REPRESENTATIVE EXPERIMENTS

reactions occurring between 600 and 1200 C follow the parabolic law. At 500 C the reaction is parabolic for about 50 min, after which it becomes nearly linear. The linear-parabolic transition with unalloyed uranium occurs between 400 and 500 C. Thus the presence of 1 a/o aluminum increases the transition temperature to about 500 C. The effect of added aluminum is too small, however, to account for the higher transition temperature reported by Hopkinson.

An additional series of runs was carried out with an alloy containing only 105 ppm of aluminum. Reaction rates were very similar to those found with the 1-a/o (1130-ppm) alloy. Tabulated rate constants for the aluminum alloys are given in

Table 46, along with previously reported values for unalloyed uranium. It is clear from the results in Table 46 that the presence of small quantities of aluminum has only a minor effect on the values of the rate constants at temperatures other than 500 C.

Table 46

RATE CONSTANTS FOR THE REACTION OF STEAM WITH
URANIUM AND URANIUM-ALUMINUM ALLOYS

Temperature (C)	Unalloyed Uranium	Uranium-Aluminum Alloy	
		105 ppm Al	1130 ppm Al (1 a/o)
<u>Linear Rate Constants, (ml H₂ STP/sq cm)/min</u>			
400	2.85 ± 0.05 ^a	-	2.2 ± 0.6
500	(Parabolic)	-	1.26 ± 0.15
<u>Parabolic Rate Constants, (ml H₂ STP/sq cm)²/min</u>			
500	4.5 ± 1.1	-	(Linear)
600	3.36 ± 0.33	5.1	3.9 ± 0.7
700	15.6 ± 1.9	-	30.3 ± 3.7
800	-	42.9	26.6 ± 0.7
900	67 ± 14	-	46.1 ± 3.4
1000	120 ± 11	69	58 ± 9
1100	-	-	139
1200	341 ± 1	469	335 ± 57

^a Standard deviations are given when more than one run was performed.

The appearance of the oxide produced in the reaction with the aluminum alloys was similar to that reported previously for uranium. The oxide formed in the linear reaction at 400 C was a brown colloidal material that was continually washed from the sample. The oxide produced by the parabolic reaction above 600 C was a glossy black material which did not flake off until the sample cubes were cooled at the end of an experiment. The oxide formed at 500 C was somewhat intermediate in character. In general, it did not flake off and did not have the glossy black appearance characteristic of oxide formed at higher temperatures.

3. Metal-Water Reaction Studies in TREAT*
(R. O. Ivins, F. J. Testa, P. Krause)

The use of the TREAT reactor at the NRTS, 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 includes metallographic and particle size evaluations.

The types of fuel specimens used are metal-clad, uranium oxide core; sintered pellets of metal and uranium oxides (cermets); and various metal-uranium alloys in the forms of pins and plates. Specimens of these materials contain sufficiently enriched uranium to raise their temperatures well above their melting points and even to temperatures of vaporization in the presence of water during a nuclear excursion.

Various observations were made during and after the transient experiments. During the transients, the pressure of the system and the temperature of the fuel (within the limits of thermocouple materials) were recorded. Samples of the gas in the system were taken to determine the hydrogen content to give a measure of the extent of reaction. Xenon-133 release to the gas phase was also determined as a measure of fission gas release. Physical observations were recorded with macrographs and micrographs, and particle size determinations were made whenever possible to record physical changes.

* The cooperation of J. Boland, F. Kirn, and H. Lawroski of the Idaho Division for the operation of the TREAT reactor is gratefully acknowledged.

a. Uranium-Water Reaction in Preheated Water

Two Zircaloy-2-clad, 93.5 weight percent uranium (20 percent enriched)-5.0 weight percent zirconium-1.5 weight percent niobium alloy pins in autoclaves were irradiated in TREAT. The autoclaves were heated prior to irradiation to a temperature of 285 C. The saturated steam within the autoclave reached a pressure of 1000 psia. In this manner the effect of temperatures and pressures, which simulated more closely those of an operating power reactor than did previous runs starting at ambient temperature, was studied.

The heated autoclave system which was loaded into a "dummy" TREAT fuel element is shown in Figure 70. Each fuel pin was contained in a vessel having a wall thickness of 0.25 in. with the initial gas seal effected by welding the vessel. The free volume of the vessel after the insertion of the fuel pin, a crucible, and fuel pin holder was 80 cc. To this, 25 cc of distilled water was added. This thin-walled vessel was, in turn, inserted in the heavy-walled autoclave shown in Figure 70, which it

fitted like a piston (tolerances allow from 0.0004- to 0.002-in. clearance on the diameter). A threaded cap on the autoclave presses on the inner vessel in order to effect containment. This assembly can withstand a high pressure.

Figure 70
HEATED AUTOCLAVE FOR TREAT
METAL-WATER EXPERIMENTS

Heavy-walled stainless tubing connections on the lighter vessel pass through the walls of the autoclave, allowing the installation of a valve for gas sampling and a pressure transducer for recording of the pressure history. In a body well in the wall of the autoclave are two chromel-alumel thermocouples, one to the controller and one to a recorder. A third thermocouple is placed between the wall of the "dummy" fuel element, used to contain the assembly in the reactor, and insulation wrapped around the autoclave assembly. Two Acrawatt "Thinband" type heaters, each rated at 850 w for 115-v AC, supply the energy required. The power to the heaters is turned off with the initiation of a TREAT transient.

The results of these two experiments (CEN-102 H and CEN-103 H) are summarized in Table 47. Figures 71 and 72 are photographs showing the fuel material after the transients. Partial melting of the core and cladding from CEN-102 H can be seen in Figure 71. The cladding bulged and ruptured, and the pin reacted to the extent of 19.1 per cent of the clad and core. The partially intact cladding and some solidified core material can be seen in Figure 72, which is a photograph of residue from the transient of higher energy. This pin reacted to the extent of 39.9 percent, based on the total reaction of the clad and core. An abundance of the black uranium dioxide is apparent in the photograph.

Table 47

TREAT TRANSIENTS CONDUCTED IN 285 C WATER (1000 psia PPESSURE) ON ZIRCALOY-2 CLAD
93.5 Wt % URANIUM (20 PERCENT ENRICHED) 5 Wt % ZIRCONIUM 1.5 Wt % NIOBIUM PINS
Core size was 0.2 in. diam x 0.5 in. length
Clad was 20 mils thick

TREAT Transient	Fuel Wt (g)		Reactor Characteristics		Energy ^a Input (cal/cm of core)	Est Peak Fuel Temp (°C)	Peak Pressure Rise (psia)	Xe ¹³³ Release ^b (% Produced)	Extent ^c of Peak rxn (Percent)	Observation
	Core	Clad	Period (min)	Integrated Power (W sec)						
CEN 102 H	3.93	0.93	139	84	90	~1150	160	26	19.1	Clad ruptured axially Core partially melted
CEN 103 H	3.71	0.91	140	180	170	>2000	710	~100	39.9	Pin completely melted and fragmented d _{av} = 0.15 in ^d

^aEnergy input values were based on natural uranium foil Zr⁹⁵ analysis and include the energy supplied by the electrical heating system (i.e. ΔH for 30°C to 285°C)

^bThe total xenon-133 production was calculated from the total fissions and a fission yield of 6.62 percent

^cDetermined by volumetric analysis of hydrogen evolved. Total percent reaction based on complete reaction of both core and clad material

^dd_{av} = average particle diameter

Figure 71

FUEL PIN AFTER TREAT TRANSIENT CEN-102 H

Pin after Removal from Autoclave

Longitudinal Cross Section
of Pin Mounted in Lucite.

Figure 72
FUEL PIN FRAGMENTS AFTER TREAT
TRANSIENT CEN-103 H

In Figure 73, the extent of reaction in the high-pressure transients may be compared with the percent reaction of pure uranium and alloyed pins in previous low-pressure transients. The extent of metal

Figure 73
URANIUM-WATER REACTION IN
IN-PILE EXPERIMENTS (TREAT)
AT "HIGH" PRESSURE

reacted with the autoclave initially at 285 C is much greater than for transients initially at ambient temperatures (~ 30 C). Two reasons for this increase in reaction are possible. Either the reaction kinetics may differ under the two conditions, or the pin might react at greater rates in the high-temperature water with a large fraction of the reaction (i.e., corrosion) occurring after the transient. Increased reaction in heated water was reported by Baker and Just for zirconium (see ANL-6548) and by Baker and Warchal for uranium (see ANL-6413, page 174). The increased reaction was a result of a higher rate of counterdiffusion of steam and hydrogen in the early stages of oxidation.

Approximately 4 hr are required for the system to cool to a temperature below 100 C. In calculating the extent of reaction that would be expected if corrosion occurred during cooling of the autoclave from 285 C to 100 C, a corrosion rate from the literature⁵⁶ of 10.2 (mg/cm²)/day (at 290 C) was used. This is the corrosion rate for uranium-5 w/o zirconium-1.5 w/o niobium alloy quenched from the gamma-phase region. (Metallographic examination indicates that this is the condition of the fuel pin after a transient.) Figure 74 shows the particle size distribution for CEN-103 H. When the percent reaction for CEN-103 H was calculated with the use of the above corrosion rate and the measured average particle size diameter (d_{sv}) of 11.5 mils, a value of 1.9 percent was obtained. Therefore, a kinetic rate difference rather than post-transient corrosion is the probable cause of the increased extent of reaction at high temperatures.

Figure 74
PARTICLE SIZE DISTRIBUTION
FOR FUEL FROM CEN-103 H

b. Zirconium-Water Reaction in Room-temperature Water

In order to use the in-pile technique to study the zirconium-water reaction, two types of fuel samples have been used. One type, used in

⁵⁶Draley, J. E., High Temperature Aqueous Corrosion of Uranium Alloys Containing Minor Amounts of Alloying Elements, in AEC-EURATOM Conference on Aqueous Corrosion of Reactor Materials, Brussels, Belgium, TID-7587, Oct. 1959, page 394.

previous work, is a zirconium-clad (Zircaloy-2) oxide-core, cylindrical pin. The results obtained with this material have been discussed in ANL-6250. A problem with this material is that of determining the amount of energy transmitted to the cladding from the core where the fission energy originates.

In comparing the in-pile studies with laboratory experiments, two methods of determining the energy are being used. The first is a direct measurement with thermocouples of the temperature of the fuel pin. This method is limited to temperatures below the melting point of the thermocouple materials used and below the melting temperature of the cladding, because the melting of the clad causes the thermocouple to lose intimate contact with the specimen. The second method is indirect. A computer is used to solve, simultaneously, the equations of heat transfer, reaction kinetics, and nuclear heating for the fuel pin. Neither method has as yet proved to be completely satisfactory. The energy input to the material has been reported as the nuclear energy imparted to the core material, and an estimate of the peak temperatures reached by the cladding has been made, based on the two methods discussed above. Improvements of computer technique and temperature measurements are expected to improve the estimate of peak cladding temperature.

A second type of sample material, used in the past quarter, is unclad, 89.35 weight percent zirconium, 10.65 weight percent uranium (fully enriched) alloy in the form of plates. When this material is subjected to nuclear excursions, the nuclear energy is generated in the fuel plate, which is the material of interest, and the determination of energy input is direct. For the determination of peak temperature, however, either direct measurement or calculation with a computer to determine the heat losses and energy contribution of the metal-water reaction is required. A second problem exists when data obtained with alloy materials are to be compared with the reaction of pure materials. However, since both types of fuel specimens used in this study were typical of actual reactor materials, the experimental data obtained can be applied directly to reactor situations.

Two additional transient irradiations (CEN-100 and CEN-101) of the alloy plate material have been conducted. Results are presented in Table 48 and are compared with results of the three previous experiments discussed in ANL-6569, page 153. The five experiments are arranged in order of increasing input of nuclear energy.

The input of nuclear energy to the fuel was determined from the zirconium-95 fission analysis of 5-mil-thick, natural uranium foils which were placed in each experimental assembly. From the average flux of 2.8 ± 0.1 fissions per microgram uranium-235 per watt-second determined from several of these foil analyses and from the calculation of the total perturbation from the data of Lewis,⁵⁷ $f = 0.71$ (ratio of average effective

⁵⁷ Lewis, W. B., Flux Perturbations by Material Under Irradiation, Nucleonics 13 (10), 82 (1955).

flux to unperturbed flux), the energy input to a fuel plate was calculated to be 1.37 (cal/gram)/Mw-sec. For another measurement of energy input, three of the plates were totally dissolved, after which burnup was determined by means of a zirconium-95 analysis. Results obtained by the two measurements agree, with deviations being less than 10 percent (see Table 48).

Table 48

SUMMARY OF THE RESULTS OF METAL-WATER MELTDOWN EXPERIMENTS CONDUCTED IN TREAT
ON ZIRCONIUM-URANIUM ALLOY FUEL PLATES, UNCLAD

Initial Test					
Conditions: H ₂ O at 25 C under 20 psia pressure of helium.					
Fuel Plates: 1 x 0.5 x 0.1-in. plates, unclad alloy (submerged in H ₂ O) of 89.35 w/o Zr and 10.65 w/o U, 93 percent enriched, total weight of each plate = 5.5 g.					
TREAT Transient					
<u>Reactor Pulse</u>	<u>CEN-100</u>	<u>CEN-87</u>	<u>CEN-88</u>	<u>CEN-89</u>	<u>CEN-101</u>
Integrated Power (Mw-sec)	208	251	372	458	573
Peak Power (Mw)	1060	1055	1140	1080	2470
Period (ms)	80	83	79	79	52
<u>Energy Input (cal/g)</u>					
Natural U foils by Zr ⁹⁵ analysis	284	341	508	626	783
Fuel pin by Zr ⁹⁵ analysis	-	320	505	583	-
<u>Results</u>					
Measured Peak Temp (C)	989	555	220	>1500	924
Estimated Peak Temp (C)	1840 (m.p. Zr)	2000	2200	2500	3600
Peak Pressure ^a (psia)	83	90	150	195	587
Appearance of fuel after irradiation	Solidified puddle of metal found in the bottom of each inner alumina crucible. Particles fused to the autoclave cap in CEN-89.				Solidified metal adhered to the broken alumina inner crucible, outer metal crucible, and supports.
Xe ¹³³ release (% total Xe produced by fission)	12.9	4.0	14.8	9.2	59.8
Extent of Metal-Water Reaction (percent of metal reacted)	6.0	5.2	9.5	11.5	67.2

^a Pressure rises were smooth with no spikes, pulses or unusual effects other than normally noted radiation effects.

The percent of metal reacted, determined by measuring the amount of hydrogen produced, is plotted in Figure 75 as a function of total nuclear energy induced. These data compare favorably with results of condenser-discharge experiments reported by Baker and Just (see ANL-6548, page 14) for zirconium-water reactions in unheated water. Their results show an increase in reaction above 2600 C due, possibly, to the melting of oxide coating which allows breakup into finer particles and furnishes additional fresh metal surface for reaction. Their results tend to agree with the results of these experiments in TREAT.

Figure 75

TREAT ZIRCONIUM-WATER 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.)

Figure 76 shows the fuel material remaining after Experiment CEN-100, which was typical of the four experiments at lower energy which yielded relatively lower extents of reaction. The material formed a

Figure 76

FUEL SPECIMEN AFTER TREAT TRANSIENT CEN-100
 (Original Fuel Plate was 1 in. x 0.5 in. x 0.1 in.)

single globule in the bottom of the inner alumina crucible. Figure 77 shows remnant particles from CEN-101, the high-energy, high-extent-of-reaction experiment. In this experiment, the zirconium-uranium plate fragmented violently, causing the inner alumina crucible to break also. Metallic particles were found adhering to alumina crucible fragments and to stainless steel supporting parts of the autoclave assembly. No fine powdery deposits were found on the surfaces of the autoclave, which indicates that no vapor-phase reaction had taken place. These observations are consistent with the mechanisms of reaction proposed by Baker and Just (loc. cit.). Since breakup of the specimen occurred in only one of

the five experiments and since the particles produced in that transient adhered to the alumina crucible fragments and to various metal parts of the autoclave assembly, particle size distributions could not be measured.

Figure 77

FUEL SPECIMEN AFTER TREAT TRANSIENT CEN-101

(Above: Alumina Crucible and Fuel Material.
Below: Metal Crucible and Holder with Fuel Material).

In none of the experiments was the pressure rise explosive. The response of the pressure transducer can be attributed almost totally to effects of irradiation of the transducer in all but the most energetic transient. In that transient, there was a definite increase in pressure; however, it was not explosive but gradual.

The amount of xenon-133 released to the gas phase was measured by counting a sample of the gases. The data are presented as percentages of the total xenon-133 produced by fission at the time of the transient and are included in Table 48.

V. ENERGY CONVERSION*

Two methods of converting nuclear energy into electricity are being studied. One method involves the use of regenerative emf cells. The other method concerns itself with studies in thermoelectricity.

A. Regenerative Emf Cell

(C. E. Crouthamel, M. Foster, C. E. Johnson, R. Heinrich, R. Eppley, S. F. Banaszek)

Studies are continuing leading to the development of a regenerative cell to convert heat into electricity in a closed cyclic system. The systems which are currently being investigated involve fused salt electrolytes with a liquid metal anode and cathode, all of which are very reactive with an ordinary atmosphere. All the cell systems currently under study may be considered as bimetallic cells with lithium and a more noble metal. The lithium hydride cell, however, is unique in that the cathode component, hydrogen, is a gas, whereas in the other cells the cathode components are liquid metals. Hydrogen also has the unique property of diffusing through certain solid metal diaphragms at a rapid rate, and attempts are being made to exploit this property in the cell design. It is anticipated that diaphragms will also be useful in the regeneration cycle as a means of separating hydrogen from other gaseous components in a highly purified state. These bimetallic systems also differ in the phase in which the cell product is deposited. In the lithium-hydrogen cell, the cell product lithium hydride is formed in the electrolyte and distributes between the molten electrolyte and molten lithium metal phases. In the other bimetallic cells, there are three liquid phases, the molten lithium anode, fused salt electrolyte, and molten cathode metal. In these cells the product appears in the molten cathode metal and the cell emf is simply that of a concentration cell.

All of the cell systems of interest in the regeneration cell program involve fused salt electrolytes and liquid metals which are not compatible with ordinary air atmospheres. In order to accomplish the experimental work without serious contamination of these reactive systems, a continuous helium gas-purification system has been placed in operation. This system purifies and recirculates gas from a small dry box at 5 ft³/min. Gas purity from the box is shown to be high, i.e., less than 30 ppm of total contaminants. A larger second unit is being completed to meet the needs of the bimetallic and lithium cell programs.

Vanadium metal shows a very high hydrogen solubility and is expected to diffuse hydrogen through the metal at high rates. This would then be expected to make a diaphragm for a hydrogen-hydride gas electrode capable of the desired high current density. Attempts have been made to

*A summary of this section is given on pages 15 and 16.

determine the diffusion rate of hydrogen through vanadium foils. These attempts have been unsuccessful due to failures of the welds at the joining of vanadium, 10-mil diaphragms to stainless steel holders.

A new bimetallic emf cell has been designed to yield thermodynamic information on alloys of lithium with tellurium, bismuth, tin, lead, zinc, cadmium, gallium, thallium and indium.

1. Inert Atmosphere Purifier

It has been pointed out previously (see ANL-6543, page 195) that the liquid alkali metal and fused salt systems under investigation in the regenerative cell energy-conversion program require an extraordinarily pure inert atmosphere for successful experimental work.

The unit described in ANL-6543, page 197 has been tested. The test revealed that the countercurrent heat exchanger, where incoming helium gas was cooled by the exit-gas stream, operated very inefficiently. Under equilibrium conditions (steady flow of helium at approximately 5 cfm), the input helium temperature to the low-temperature activated carbon bed used for final removal of gas contaminants was -90 C and the exit temperature was -135 C. Proper operation of the bed requires a gas temperature of -190 C throughout the carbon bed. The countercurrent heat exchanger was removed and replaced by a 40-ft copper coil ($1\frac{1}{8}$ -in. OD, 1-in. ID) immersed in liquid nitrogen. This coil, which acted as a precooler for the helium gas entering the carbon bed, was tested in operation, and the temperature of the helium entering the carbon bed was measured at -190 C. Under these conditions and at a helium circulation rate of 5 cfm, 200 liters of liquid nitrogen was required per 12 hr of operation of the precooling unit.

The box atmosphere was analyzed by means of a Consolidated Electrodynamics Corporation moisture monitor.* In this instrument, a phosphorus pentoxide surface in which two platinum coils are buried absorbs water from the helium stream and continuously electrolyzes the water to hydrogen and oxygen. The electrolysis current is directly related by Faraday's law to the mass rate of flow of water into the phosphorus pentoxide cell and is used to indicate the water content of the helium. Full-scale range of the monitor was 1 to 100 ppm water.

A second method of atmosphere monitoring was observation of the duration of a mirror NaK liquid surface or bright lithium metal surface. A mirror duration⁵⁸ of 30 min was taken to indicate roughly an integrated

*Consolidated Electrodynamics Corp., 360 Sierra Madre Villa, Pasadena, California. Moisture monitor number 26-303MB range 0-100 ppm by volume H₂O.

⁵⁸Glove Boxes and Shielded Cells, Proceedings of the Symposium on Glove Box Design, pp. 127-130, Academic Press Inc., New York (1958).

level of impurities, such as water, O_2 , N_2 , H_2 , and CO_2 , of 50 ppm or less. A 30-min duration of the mirror was easily achieved. A lithium bright metal surface was maintained for several days.

The actual water content was measured at 2 ppm by means of the phosphorus pentoxide moisture monitor. During an extended period of hand operation (2 hr) in the neoprene rubber gloves, the water content never exceeded 6 ppm. It is assumed that the diffusion of water from the hands has approached an equilibrium value with the system in this time. When the box is not in use, metal covers are placed over the glove ports.

A second helium-purification system is nearing completion. This system will use a larger Rotron* multistage blower than that used in the first unit as a helium gas pump capable of maintaining a flow rate of 10 cfm. Two 35-ft copper heat exchanger coils, of one-inch internal diameter, were suspended in the cold nitrogen vapor, and on the helium input an additional 35-ft coil was placed under the nitrogen liquid in the tall Dewar flask.

It was found that without a helium heat exchanger, cooling a 10-cfm helium stream to $-195^\circ C$ with a long copper coil immersed in liquid nitrogen required 800 liters of nitrogen per 24 hr of operation. The liquid nitrogen consumption was reduced to 100 liters per 24 hr by use of the heat exchanger. Since the cost of liquid nitrogen to the laboratory is seven cents per liter, the 100 liters per 24 hr amounts to a cost of \$7.00. Since it is not necessary to run the purification unit on a continuous basis, it is believed that this expense is not too great.

2. Phase Studies by Heating and Cooling Curves (C. E. Johnson and S. Banaszek)

Information is needed for various systems that make up the lithium hydride fuel cell. It is of importance in the operation of this fuel cell to know the phase diagrams of the systems involved. These data will allow the maximum concentrations of lithium hydride and the minimum temperatures to be set, which will eliminate the problems of solid-phase formation. In addition, these data can be used to determine the approximate activities of lithium hydride in the fused salts. It is planned initially to study the lithium hydride-lithium chloride and lithium hydride-potassium chloride binary mixtures and possibly the lithium chloride-potassium chloride-lithium hydride ternary mixtures in order to collect some of the needed data.

Apparatus specifically designed for the collection of freezing point data has been assembled and tested. The furnace tube is connected directly into an inert-atmosphere box so that reactive salts and metals can

*Rotron Manufacturing Co., Woodstock, New York.

Figure 78
HEAT AND COOLING
CURVE SAMPLE
ASSEMBLY

be weighed and introduced into the sample holder without contamination. A diagram of the assembly that holds the sample is shown in Figure 78. The sample is placed in a metal crucible which in turn is placed within the firebrick container. The firebrick is totally enclosed in 316 stainless steel and thus is inert to the sample environment. Two thermocouples are placed in the central well extending into the sample crucible, and one thermocouple is placed in the well immediately outside the firebrick. One of the central thermocouples is used to measure the sample temperature directly. The other central thermocouple and the thermocouple outside the firebrick enclosure are used to provide a differential emf to operate a differential dc amplifier. This amplifier controls the heating rate and cooling rate of the sample. All components except the thermocouple well tips are made of 316 stainless steel. The thermocouple well tips are made of 347 stainless steel which has been demonstrated to be very corrosion-resistant to lithium hydride and molten lithium.

Briefly, the electronic portion of the apparatus consists of the following components. An adjustable-span, adjustable-suppression recording potentiometer is used to record the temperature of the melt. All temperatures are measured by platinum-platinum, 10 percent rhodium thermocouples. Power to the furnace surrounding the sample is supplied by a saturable-core reactor. Voltage for the saturable-core reactor is supplied by a magnetic amplifier which is controlled by a proportionating controller. Input to the recorder-controller is supplied by a differential dc amplifier. The signal to the differential amplifier comes from the difference in voltage between the thermocouple located in the melt and that located immediately outside the firebrick surrounding the sample. Heating and cooling rates may be changed markedly by adjusting the differential amplifier to maintain anywhere from one microvolt to five millivolts differential between the two thermocouples.

Typical data obtained using this apparatus for a well-known system are shown in Figure 79. This is a cooling curve for a melt composed of 70.97 mole percent lithium chloride and 29.03 mole percent potassium chloride. A sharp break was obtained at 450 C for the liquid-liquid to liquid-solid transition (freezing out of lithium chloride). The flat portion of the curve at 350 C represents freezing of the eutectic. Since the

literature values for these transitions are 450 C and 352 C, agreement with the literature values⁵⁹ is very good.

Figure 79

COOLING CURVE FOR LITHIUM CHLORIDE-
POTASSIUM CHLORIDE MELT

3. Hydrogen Diffusion through Metals
(R. Heinrich)

The lithium hydride cell will require a gas electrode made of a reliable material. Iron has the important property as a hydrogen-diffusion diaphragm of being easily regenerated in a hydrogen atmosphere at about 650 to 700 C (i.e., diffusion-hindering oxide films can be removed). This is because iron oxides are reduced to iron by hydrogen at these temperatures. Previous experiments have indicated that pure iron diaphragms are compatible with the cell environment but that rates of hydrogen diffusion through a 10-mil-thick, pure iron diaphragm are too slow by a factor of about 100. Alpha ionization of the hydrogen behind the diaphragm was found to double the rate; the diffusion rate was found to increase by a factor of 1.5 in a loaded cell as compared with rates with a vacuum on the discharge side of the diaphragm; and finally it is estimated that the iron diaphragm thickness can be reduced to 2.5 mils to give a fourfold increase in diffusion rate. Altogether, the diffusion rate would increase by about a factor of 10, which would still be a decade short of the desired rate.

The other diaphragm metals which might be compatible with the cell environment and through which hydrogen diffuses at rates of 10-100 times the rate through iron in the temperature range from 400 to 500 C are:

⁵⁹Elchardus, E. and Laffitte, P., Bull. soc. chim., France, 51, 1572 (1932).

vanadium, tantalum, and niobium. Each of these metals shows a marked decrease in hydrogen diffusion when the surface becomes oxidized, and this oxide is very difficult to remove. In a single experiment, vanadium was regenerated repeatedly by heating to 750 C in a high vacuum. When the diaphragm holder was opened, vanadium oxide was found to be deposited over a wide area of the system.

Although vanadium is known to dissolve in fluoride salts, not enough is known about its behavior in other salts to eliminate it as a possibility. No consistent data for hydrogen diffusion have been obtained on vanadium because all-welded diaphragms developed leaks, either immediately or after a few temperature cycles in making the measurements of hydrogen diffusion. The diaphragms have been joined to stainless steel or pure iron holders and leaks develop at the joint.

A contract has been negotiated with the Battelle Memorial Institute to study the problem of bonding various diaphragm materials to both cells and rings suitable for making the measurements of hydrogen diffusion.

4. Bimetallic Cells (M. Foster)

Preliminary experiments to determine the magnitude of the voltages and the current characteristics of several bimetallic cells have been reported in the past (see ANL-6477, page 209 and ANL-6543, page 200). The bimetallic cell appears to have a very low current polarization and can be constructed with very low internal resistance. It is expected that operating currents would be 400 ma/cm² and over. No extensive experimental work has been carried out on regeneration. Patents, however, have been applied for by us for the electrical regeneration of these systems. In this scheme, the cells would be operated in reverse at high temperature, hopefully at a lower voltage. These experiments all involved the use of liquid lithium as the anode and one of the following as the liquid cathode: tellurium, selenium, bismuth, tin, lead, zinc, or cadmium. The results obtained warranted a new series of experiments designed to yield thermodynamic information. With this in mind, a new liquid metal emf cell has been constructed.

In the new cell, liquid lithium and various lithium alloys previously mentioned will be contained in covered porous pure beryllia crucibles (porosity 30 to 50 percent, pore size approximately 50 μ). These porous cups will be suspended in such a manner as to contact the fused salt electrolyte, which will probably be the eutectic of lithium and potassium chlorides. The electrolyte will be contained in a covered tantalum crucible in a stainless steel shell connected to an inert-atmosphere dry box. All electrical contacts in the cell will be either tantalum or platinum. The latter will be used only when necessary (as in the case of tellurium and

selenium liquid cathodes), and then the contact will be connected to tantalum while in the heated proximity of the cell in order to avoid the risk of thermal effects.

In addition to the liquid cathode materials previously mentioned, gallium, thallium, and indium will be run. To this end, lithium of 99.99 percent purity and other metals of 99.99+ percent purity have been obtained.

The previous work was also limited by the lack of a good inert-atmosphere box of high enough purity. The second helium-purification unit is being completed (as discussed in the first section) and is expected to meet this need.

B. Thermoelectricity Research (R. K. Edwards, H. M. Feder)

Studies in thermoelectricity are underway to contribute to the technological development of direct conversion of heat energy from nuclear reactors into electrical power by means of the thermocouple effect.

Two limited materials areas are under study. These are liquid thermocouple systems and refractory solid thermocouple materials. The latter are considered to be of particular interest to reactor energy conversion.

1. Liquid Systems (R. K. Edwards, C. Metz)

The thermoelectric properties of liquid systems are of importance since their study should contribute to the extension of solid-state theory to the liquid state. Solid-state investigations of the transport properties of binary semiconductors are generally limited to very narrow composition ranges by virtue of narrow ranges of phase stability. Liquid binary systems offer a greater latitude for the study of composition dependencies. The liquid studies are directed toward obtaining systematic data which might lead to correlation and understanding of the factors pertinent to the controlled modification of electronic structures in metallic or semimetallic systems toward more favorable thermoelectric properties.

During the past quarter, Seebeck coefficients in the liquid indium-antimony system have been measured for 24 compositions in the range from 100 to 46 atom percent antimony for the mean temperature 750 C. Before the data are reported, they must be more thoroughly examined in view of a correction term which arises as a result of a residual emf found for zero temperature difference between the hot and cold junction temperatures. The correction term, while not expected to influence the relative values within the set of data, will be important in establishing the

absolute values. The procedure used in this study was the same as that used in the liquid indium-bismuth system discussed in the previous quarterly report (ANL-6569, page 157).

In brief, liquid antimony has a positive Seebeck coefficient, and this value rises only slightly as indium is added to a composition of about 45 atom percent indium. Thereafter, as the indium content is increased to about 54 atom percent, the Seebeck coefficient values decrease and in this range are in generally good agreement ($\pm 0.2 \mu\text{V}/\text{C}$) with the values obtained in the tentative study (see ANL-6477, page 214) performed at the mean temperature 630 C. However, in contrast with the earlier study, no definite evidence of unusual behavior at the 50 atom percent composition has been found in the current study. The general experimental procedures were the same in the two studies; however, the earlier study had been termed "tentative" because a different geometrical arrangement of the electrodes led to less carefully defined temperature zones. Drawings of the apparatus will be presented in a later report. The remaining composition range will be studied for the mean temperature 750 C.

Errata

In ANL-6569, the preceding Chemical Engineering Division summary report, on pages 157 and 159, the graphs but not the titles were transposed in Figures 57 and 58. For Figure 57, read the graph in Figure 58, and add the following key to the symbols:

- Triangle. Set of measurements for which compositions were successively altered right to left.
- Square. Set of measurements for which compositions were successively altered left to right.
- Circle. Set of measurements for which compositions were successively altered left to right.

For Figure 58, read the graph in Figure 57.

2. Refractory Solid Thermocouple Systems (M. Tetenbaum, F. Mrazek)

For use at high temperature, a refractory broad-band semiconductor is required if thermoelectric properties are to be favorable over a large temperature interval. The lanthanide and actinide sulfide systems are highly refractory and have phases with electron concentrations in the semiconducting range. The uranium and thorium sulfide systems and their solid solutions have been selected for the initial studies.

Measurements of the Seebeck coefficient as a function of temperature have been made with uranium monosulfide containing approximately

one percent by weight insolubles, presumably uranium oxysulfide. The uranium monosulfide specimen was an irregularly shaped sintered ingot.

Figure 80
ABSOLUTE SEEBECK COEFFICIENT VS. TEMPERATURE FOR VARIOUS SPECIMENS OF URANIUM MONOSULFIDE

*See Footnote 60 below.

The results are shown in Figure 80. Curve 1 shows measurements made in the temperature range from 100 to 900 C. A leak developed in the vacuum system after completion of the Seebeck coefficient measurement at 750 C. The surface of the uranium monosulfide ingot was found to be tarnished upon removal from the apparatus. The sudden drop-off in the value of the Seebeck coefficient at 875 C can therefore be attributed to partial oxidation of the sample.

Seebeck-coefficient measurements of the specimen were resumed after attempts were made to remove the surface coating from the ingot. The results are shown as Curve 2 in Figure 80. For comparison, measurements reported in the previous quarterly (ANL-6569, page 159) for uranium monosulfide containing approximately five percent by weight uranium oxysulfide (see Curve 3) and in addition measurements reported by Electro-Optical Systems, Inc.⁶⁰ on a melted uranium monosulfide specimen of undefined composition also are shown on Figure 80. These data suggest that bulk oxidation of the uranium monosulfide ingot occurred when the leak developed in the vacuum system, and that oxidation of uranium monosulfide results in a lowering of the Seebeck coefficient value.

It is interesting that a somewhat similar oxidation was reported by Carter, Miller, and Ryan⁶¹ for the cerium sulfide system. Their early results showed a maximum in the Seebeck coefficient near 700 C, and a rapid deterioration in electrical properties with higher temperatures, presumably due to contamination of their samples with boron and oxygen (boron nitride was used as an insulator in their apparatus). When their heating cycle time was decreased, better high-temperature results were obtained.

⁶⁰Jordan, C. B., High-temperature Semiconducting Compounds for Thermoelectric Power Generation, Final Comprehensive Report, Dec. 15, 1960 through Dec. 15, 1961, EOS-1592 - Final, Electro-Optical Systems, Inc., Pasadena, California, p. 19, January 15, 1962.

⁶¹Carter, F. L., Miller, R. C., and Ryan, F. M., Advanced Energy Conversion, 1, 165 (1961).

No Hall voltage was detected* on a thorium monosulfide plate fabricated from an arc-melted ingot. The resistivity, measured in the Hall apparatus at room and liquid nitrogen temperatures, was found to be 180×10^{-6} and 75.6×10^{-6} ohm-cm, respectively. Room-temperature resistivity values of the specimen ranging from 180×10^{-6} to 200×10^{-6} ohm-cm were reported by us previously (see ANL-6543). It appears that the thorium monosulfide specimen has a positive coefficient of resistivity, which confirms the metallic nature of this material.

The Seebeck coefficient values shown in Figure 80 are lower than the values reported for the refractory cerium sulfide system ($S/Ce \cong 1.4$). However, the usefulness of uranium monosulfide as a thermoelectric material can only be ascertained after obtaining electrical and thermal conductivity data.

*These measurements were made by Manuel Kanter and C. W. Kazmierowicz of the Solid State Division.

VI. DETERMINATION OF NUCLEAR CONSTANTS*

(C. Crouthamel)

Knowledge of fast-neutron cross sections is necessary to the fast reactor program. Neutron cross sections are being studied by means of monoenergetic neutrons and by means of neutrons produced in a fast reactor. The monoenergetic-neutron work includes the measurement of capture and total cross sections as a function of neutron energy. In the present program neutron capture cross sections are being measured for thorium-232. Determinations of the ratio of the capture-to-fission cross section, α , of uranium-233 in EBR-I, Mark III, are reported. In addition the number of $(n, 2n)$ reaction events in this batch of uranium-233 are reported.

A. Fast-neutron Capture Cross Sections of Thorium-232 (D. Stuepgia, A. Smith,** and K. Hamm[†])

The fast-neutron capture cross section of thorium-232 is being measured as a function of neutron energy in the range from 0.2 to 1.2 Mev. Thorium-232 is the fertile isotope in the uranium-233 reactor fuel cycle, and its capture cross section in this energy range is important in the estimation of the breeding ratio of this system. The energy range that is being studied corresponds to that of a fast reactor neutron spectrum. The presently available data^{62,63,64} on the cross section of thorium-232 show significant disagreement both in shape and absolute value. The present work seeks to clarify this situation.

The capture cross section of thorium is being measured by determining the absolute disintegration rate of the thorium-233 produced in a thorium target of known mass irradiated in a monoenergetic neutron beam of known flux. The irradiations were carried out at the Reactor Engineering Division's Van de Graaff accelerator, in which the proton beam produced neutrons by means of the $\text{Li}^7(p,n)\text{Be}^7$ reaction. Thorium was separated from its daughter products, and target samples were made by pressing thorium dioxide into one-centimeter-diameter discs of about 0.3 g. The targets were mounted in a fission chamber, which monitored the neutron flux by counting fissions in a thin sample of enriched uranium. The activated thorium targets were counted in an end-window proportional counter,

*A summary of this section is given on page 16.

**Reactor Engineering Division.

[†]Resident Research Associate, Carthage College.

⁶²Hanna, R. C., and Rose, B., J. Nucl. Energy, 8, 197 (1959).

⁶³Hughes, D. J., and Schwartz, R. B., Neutron Cross Sections, BNL-325, 2nd Ed. (1958).

⁶⁴Lane, A. M. and Lynn, J. E., Proc. Phys. Soc. A70, 557 (1957).

and the 23-min beta decay of the capture product, thorium-233, was followed over several half-periods.

In order to relate the beta-counting data to an absolute disintegration rate, a calibration was made based upon absolute beta counting. This calibration was accomplished by spiking a thorium dioxide target sample with a sample of thorium-233 of known disintegration rate, as determined by 4π beta counting, and then counting the spiked target in the proportional counter, in the same geometry in which the monoenergetic neutron-irradiated targets were counted.

Figure 81
NEUTRON CAPTURE CROSS
SECTION OF THORIUM-232

Figure 81 includes the experimental results of these measurements and of past work, giving the data of Hanna and Rose⁶² and of Hughes and Schwartz.⁶³ The theoretical prediction of Lane and Lynn⁶⁴ is also shown. Above 600 kev, the results of this work are in qualitative agreement with other measurements, excepting the results of Hanna and Rose. The present work shows an increase in the capture cross section of thorium-232 in the vicinity of 800 kev. This rise is in good agreement with the prediction of Lane and Lynn which considers only the effect of lower-lying en-

ergy levels of thorium-232. The qualitative effect of inelastic scattering to the next available residual nuclear states at about 800 kev and 1100 kev reported by Smith⁶⁵ will be a decrease in the cross section above 800 kev. This decrease is found in the present work.

B. Capture, Fission, and (n,2n) Reactions in EBR-I (C. E. Crouthamel, R. R. Heinrich, G. H. McCloud)

The first report of data from the EBR-I Mark III irradiations was made in the previous quarterly (ANL-6569, page 162). The significance of these data to the fast breeder reactor program was also discussed. The Mark III loading is very similar to Mark II and was fabricated from a highly enriched uranium-2 percent zirconium alloy slug coextruded with a 0.020-in. zirconium jacket. Natural uranium-2 percent zirconium alloy sections were

⁶⁵Smith, A. B., Phys. Rev., 126, 718 (1962).

fabricated in a similar manner for the inner blanket. A detailed description of this core has been given by F. W. Thalgott *et al.*⁶⁶

The data presented herein extend the previous data in two respects. First, in the uranium-233 irradiations, the number of (n,2n) reactions per 10^6 uranium-233 atoms have been added to the previously reported fission and capture data as a function of the reactor horizontal and vertical positions. These data are given in Table 49. Second, the alpha values obtained in EBR-I, Mark I irradiations for uranium-235 and plutonium-239 have been repeated in Mark III. The EBR-I, Mark I data were reported by Kafalas, Levenson, and Stevens.⁶⁷ The new data indicate several discrepancies in the old; however, the two sets of data check very well for the most part. These discrepancies are discussed below.

Table 49

FISSION, CAPTURE, AND (n,2n) REACTIONS IN EBR-I, MARK III LOADING
URANIUM-233 IRRADIATION

Mark III loading is a highly enriched uranium-2% zirconium alloy core clad in a 0.020-in. zirconium jacket. See Ref. 67 for details about reactor geometry.

Reactor Position Horizontal (in.)	Reactor Position Vertical (in.)	Alpha Activity Ratio $\frac{U^{232}}{U^{233}} \times 10^3$	Reactions per 10^6 U^{233} Atoms				
			Fissions	Captures	(n,2n)	$\left(\frac{n,2n}{\text{fissions}}\right) \times 10^4$	$\left(\frac{n,2n}{n,\gamma}\right) \times 10^2$
0.5		2.02	1488	81.1	0.923	6.20	1.14
1.25		1.74	1422	79.0	0.795	5.59	1.01
2.15		1.73	1329	73.3	0.791	5.95	1.07
3.0		1.33	1189	66.6	0.608	5.11	0.913
3.80		1.03	1018	65.4	0.471	4.63	0.720
4.60		0.417	737.5	55.5	0.191	2.59	0.344
	-5.88	0.235	533.3	41.7	0.107	2.01	0.257
	-3.88	0.712	896.9	55.2	0.325	3.62	0.589
	-1.89	1.53	1293	72.2	0.699	5.41	0.968
	0.08	1.74	1422	79.0	0.795	5.59	1.01
	2.02	1.46	1354	73.6	0.667	4.93	0.906
	3.95	1.18	1091	61.7	0.539	4.94	0.874

The number of (n,2n) events in this batch of uranium-233 could easily be determined because of the extremely high isotopic purity of the unirradiated samples. The uranium was separated from both fission and daughter products before obtaining the alpha pulse spectra with a solid-state spectrometer. The uranium-232 could not be detected in the

⁶⁶Thalgott, F. W., Boland, J. F., Brittan, R. O., Carter, J. C., McGinnis, F. D., Novick, M., Okrent, D., Sandmeier, H. A., Smith, R. R., and Rice, R. E., *Stability Studies on EBR-I*, Proceedings of the Second United Nations International Conference, 12, p 250 (1958).

⁶⁷Kafalas, P., Levenson, M. and Stevens, C. M., *Nucl. Sci. and Eng.*, 2, 657 (1957).

unirradiated control sample. Uranium-232 has an alpha group around 5.3 Mev which is well above and completely resolved from the uranium-233, 4.8-Mev alpha group. The data summarized in Table 49 correlate the number of fission, capture, and (n,2n) reaction events per 10^6 uranium-233 atoms with reactor position. The (n,2n) reactions in uranium-233 are about one percent of the capture events in the core positions.

The alpha data obtained with the Mark III loading for uranium-235 are summarized in Tables 50 and 51.

Table 50

ALPHA FOR URANIUM-235.
HORIZONTAL LOADING, EBR-I, MARK III

Sample No.	Distance from Core Center (in.)	Pile Position of Sample	Fissions per 10^6 U ²³⁵ atoms	Captures per 10^6 U ²³⁵ atoms	Alpha (σ_c / σ_f)
2	0.5	core	985.4	123.1 ± 4	0.124 ₉
10	0.93	core	980.4	122.7 ± 4	0.125 ₂
3	3.0	core	777.9	106.3 ± 5	0.136 ₆
4	5.4	inner blanket	422.9	79.2 ± 2	0.187 ₃
5	7.0	inner blanket	301.8	63.8 ± 2	0.211 ₄

Table 51

ALPHA FOR URANIUM-235.
VERTICAL LOADING, EBR-I, MARK III

Sample No.	Distance from Core Center (in.)	Pile Position of Sample	Fissions per 10^6 U ²³⁵ atoms	Captures per 10^6 U ²³⁵ atoms	Alpha (σ_c / σ_f)
16	+10.14	upper blanket	170.3	40.1 ± 2	0.235 ₅
15	+ 8.14	upper blanket	250.1	56.2 ± 2	0.224 ₇
14	+ 6.14	upper blanket	384.1	74.4 ± 3	0.193 ₇
13	+ 4.15	core	631.9	98.6 ± 4	0.156 ₀
12	+ 2.15	core	885.3	113.3 ± 2	0.128 ₀
10	+ 0.16	core	980.4	122.7 ± 4	0.125 ₂
8	- 1.84	core	901.8	112.7 ± 1	0.125 ₀
7	- 3.84	core	669.0	97.2 ± 2	0.145 ₃
6	- 5.83	lower blanket	388.7	74.0 ± 2	0.190 ₄

In the previous work only one sample was analyzed in the core for each isotope, i.e., uranium-235 and plutonium-239. The other samples which were irradiated had melted and were not analyzed for fission because of the known loss of both xenon-137 and cesium-137. However, the burnup determination in the previous work appears to be too low in the remaining reactor core sample, probably because of overheating. This weakness in the previous data in Mark I was realized and is the main reason for the additional irradiations in Mark III. A comparison of the data from the two irradiations of uranium-235 is shown in Figures 82 and 83. The agreement of the data is reasonably good everywhere except for the reactor core position. The burnup values in the horizontal positions in the inner blanket of Mark I are somewhat lower than Mark III irradiations suggesting small losses of cesium-137.

Figure 82

URANIUM-235 FISSION AND CAPTURE REACTIONS
FOR EBR-I, MARK I AND -III LOADINGS
(VERTICAL)

Figure 83

URANIUM-235 FISSION AND CAPTURE REACTIONS
FOR EBR-I, MARK I AND -III LOADINGS
(HORIZONTAL)

A similar check of the Mark I plutonium-239 irradiations was also made in the Mark III irradiation. The new alpha data for plutonium-239 are summarized in Tables 52 and 53. In comparing these irradiations,

two of the burnup analyses in the inner blanket appear to be too high in the previous Mark I analysis. These are shown in Figure 84 as the two points in the burnup analysis which do not parallel the new data. There appears to be no explanation for these two high results. The symmetry of the new data and rise in plutonium alpha value in the inner blanket strongly indicates it is the more nearly correct.

Table 52

ALPHA, FISSION, AND CAPTURE FOR PLUTONIUM-239, EBR-I,
MARK III HORIZONTAL LOADING

File Position of Sample	Distance from Reactor Axis (in.)	Fissions per 10^6 Pu^{239} Atoms	Captures per 10^6 Pu^{239} Atoms	Alpha (σ_c/σ_f)
core	1.25	1171.8	87.5	0.074 ₇
core	2.15	1106.2	81.4	0.073 ₆
core	3.00	935.7	74.4	0.079 ₅

Table 53

ALPHA, FISSION, AND CAPTURE FOR PLUTONIUM-239, EBR-I,
MARK III VERTICAL LOADING

File Position of Sample	Vertical Distance from Mid-plane (in.)	Fissions per 10^6 Pu^{239} Atoms	Captures per 10^6 Pu^{239} Atoms	Alpha (σ_c/σ_f)
upper blanket	+10.13	306.2	47.6	0.155
upper blanket	+ 6.20	519.1	59.2	0.106
core	+ 4.27 ^a	799.3	68.8	0.086 ₁
core	+ 2.31	1088.3	78.3	0.072 ₀
core	+ 0.41	1171.8	87.5	0.074 ₇
core	- 1.56	1086.9	79.1	0.072 ₈
core	- 3.54	756.2	65.8	0.087 ₀
lower blanket	- 5.54	435.0	54.4	0.125

^aAt edge of core and upper blanket.

Figure 84
CAPTURE AND FISSION REACTIONS
FOR EBR-I, MARK I AND -III
LOADINGS (VERTICAL)

VII. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, K. Bremer, B. Kullen and D. Bryant)

Routine Operations

There was a total of 69,866 gal of liquid radioactive wastes processed during July, August, and September, 1962. The volumes processed by the various methods were as follows:

<u>Process</u>	<u>Volume, gal</u>
Evaporation and Concentration	44,600
Filtration	12,250
Ion-Exchange (Cation, only)	12,250
Neutralization of HF Wastes	288
Absorption into Vermiculite	478
Total	69,866

B. High-level Gamma Irradiation Facility

(H. G. Swope, N. Ondracek, G. Teats, R. Juvinall and V. Lemke)

A summary of irradiations performed in Racks M-1 and M-2 for July through September, 1962, is given in Table 54.

Table 54

SUMMARY OF IRRADIATIONS PERFORMED IN RACKS M-1 AND M-2 DURING JULY THROUGH SEPTEMBER, 1962

<u>Month</u>	<u>Rack M-1</u>				<u>Rack M-2</u>		
	<u>No. of Samples^a</u>	<u>No. of Special Dosimetry Samples</u>	<u>Total Urn Units^b</u>		<u>No. of Urns^c</u>	<u>No. of Special Dosimetry Urns</u>	<u>Total Urn Units^d</u>
			<u>Day</u>	<u>Night</u>			
July	92	0	459	1628	1	1	22
August	797	842	2937	2486	1	1	37
September	241	317	1590	3101	0	0	0
Totals	1130	1159	4986	7215	2	2	59

^aEquivalent to a No. 2 size can.

^b1 urn unit in Rack M-1 equals 2×10^6 rad.

^cEquivalent to one 20-inch urn.

^d1 urn unit in Rack M-2 equals 2×10^5 rad.