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for Plutonium and Uranium (TID-4500)
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SUMMARY

Chemical Engineering Division Semiannual Report

I. Compact Pyrochemical Processes (pages 23 to 63)

Compact pyrochemical processes continue to be developed for the recovery of uranium and plutonium from fast breeder reactor fuels. These processes can accommodate oxide, carbide, and metal reactor fuels. To accomplish the basic separations in present process concepts, differences in the partition behavior of the fuel constituents between liquid metal and salt solvents are utilized. One of the newer concepts under development in pyrochemical processing employs a salt transport separations step. Salt transport separations are based on the selective transfer of solutes (fissile and fertile materials) from one liquid metal solution (donor) to another (acceptor) by cycling a molten salt phase which acts as a carrier between the two metal solutions. A conceptual flowsheet (see Figure I-1) employing a salt transport step for the separation of uranium and plutonium is currently under investigation. Processes utilizing salt transport separations show promise of excellent fission product removal and high recoveries of uranium and plutonium.

Supporting Chemical Studies of Pyrochemical Processes. In support of the development of liquid metal and salt systems for pyrochemical processes, chemical investigations have included (1) the determination of distribution coefficients of uranium, plutonium, and fission products between liquid alloys of magnesium and molten salts containing MgCl_2 , and (2) the determination of the solubilities of these same solutes in several liquid magnesium alloys that are being evaluated as candidate donor alloys.

Measurements of the distribution coefficients of cerium, plutonium, and uranium between molten MgCl_2 and liquid Cu-Mg alloys at 800°C were made as a function of the magnesium concentration of the alloys. The results of the measurements show that (1) the cerium partitions strongly in favor of the molten salt, (2) the plutonium partitions somewhat in favor of the molten salt at low magnesium concentrations, and (3) the uranium tends to favor the liquid alloy. In addition, a Cu-6.5 w/o Mg alloy

appears to offer excellent potential as a donor alloy for the salt transport separation step. This alloy affords the possibility of a good separation of the rare earth fission product elements from uranium and plutonium, and the indications are that the transport rates of uranium and plutonium from this alloy will be rapid.

Distribution coefficient data were also obtained for cerium, plutonium, and uranium between a salt (consisting of equimolar NaCl-CaCl_2 and varying amounts of MgCl_2) and Cu-6.5 w/o Mg alloy at 800°C . These distribution data provide a basis for the selection of an optimum concentration of MgCl_2 in the salt for the reduction of uranium and plutonium oxides by Cu-6.5 w/o Mg alloy and for the rare earth-plutonium separation. The data show a regular increase in each of the distribution coefficient curves as the MgCl_2 concentration in the salt is increased. The rare earth-plutonium separation factor (309) remains essentially constant as the MgCl_2 concentration in the salt increases from about 10 to 100 m/o MgCl_2 .

In another distribution experiment, distribution coefficients were measured for cerium, plutonium, and uranium between (Cu-50 w/o Cd)-Mg alloys (as a function of magnesium concentration in the metal phase) and MgCl_2 -30 m/o NaCl-20 m/o KCl at 600 and 700°C . The addition of cadmium to the binary Cu-Mg alloy and the use of a lower-melting salt mixture would permit a lower operating temperature for the process. A calculation made from the available data indicates that the operating temperature of the oxide reduction-partition step in the conceptual process could be dropped to 650 to 700°C (from $\sim 800^\circ\text{C}$) by using a Cu-Cd-Mg alloy instead of a Cu-Mg alloy.

Other distribution data were obtained for various solutes between MgCl_2 -30 m/o NaCl-20 m/o KCl and Cd-Zn-Mg donor alloys. In one experiment carried out at low magnesium concentration (~ 0.3 w/o) and a cadmium-to-zinc ratio of 9 to 1, the effect of temperature on the distribution coefficient for uranium was determined over the range of 448 to 650°C . The data show that uranium distributes to the salt in sub-

stantial concentrations (1.4 w/o uranium at 448°C to 9.5 w/o at 650°C). In another experiment conducted with (Cd-10 w/o Zn)-Mg alloys at 600°C, the effect of varying magnesium concentrations (up to 10 w/o) in the ternary alloy on the distribution coefficient for uranium, plutonium, and cerium was determined. The data show that the distribution coefficients of cerium, plutonium, and uranium are approximately the same for the system (90 w/o Cd-10 w/o Zn)-Mg and MgCl_2 -30 m/o NaCl-20 m/o KCl and the system Cd-Mg and MgCl_2 -30 m/o NaCl-20 m/o KCl. However, the actual solute concentrations in the metal and salt phases are much higher in the former system. Thus, a (Cd-10 w/o Zn)-low Mg/salt system may become attractive as a donor alloy where low operating temperatures are desired.

Solubility data were determined for uranium in liquid Cd-Cu donor alloys in the temperature range 550 to 650°C, and for plutonium in liquid Cu-Mg donor alloys in the temperature range 500 to 800°C. The uranium and plutonium solubilities are believed to be sufficiently high for process purposes.

In another supporting study, the liquidus temperature was determined at two compositions in the system MgCl_2 - MgBr_2 to ascertain if there is a low-temperature liquid region. Such a region would be of process interest in that the high magnesium ion concentration in the salt phase, which gives high distribution coefficients, could be maintained at lower process temperatures. No liquidus region below 700°C was found in the region of interest (MgCl_2 concentrations of 60.1 and 40.1 w/o) in this system. Therefore, a MgCl_2 - MgBr_2 system appears to offer no significant advantage over MgCl_2 alone (m.p. 716°C) as a process salt.

The first step after decladding in current pyrochemical methods for the reprocessing of oxide fuels is the reduction of the oxide from a molten salt slurry by a Cu-Mg alloy. This reaction produces insoluble MgO as a by-product in the molten salt. In order to reuse this salt, removal of most of the MgO is necessary. A supporting chemical study was, therefore, undertaken to explore a possible separation method which involves allowing the oxide particles to settle to the bottom of the salt and then decanting the supernatant salt. Characterization of the MgO particles showed them to be of a relatively uniform size; the majority were below 5 μ in diameter and the largest, about 10 μ . A test of the settling behavior of the MgO showed that a minimum of about 2 hr was required for the insoluble material to settle, leaving an essentially clear supernatant salt which consisted of about three-fourths of the total salt volume. Analyses of the two layers of the settled salt showed that the MgO in

the supernatant salt amounted to about one hundredth of that contained in the lower layer. Thus, it appears that decantation of the supernatant salt after settling of the insoluble oxide offers a possible method for recovering salt for recycle.

Isotopically pure (99.91%) ^{24}Mg metal, suitable for use in neutron-scattering and polarization experiments, was prepared by a simultaneous high-temperature (1150°C) reaction of ^{24}MgO with aluminum and CaO.

Supporting Engineering Studies of Pyrochemical Processes. The development of the engineering technology required for the separation of plutonium and uranium from fission products by extractions between liquid metal and molten salt phases was continued. Process concepts are being investigated on a pilot-plant scale, with the present emphasis being on salt transport separations. These separations are based on the selective transfer of solutes between two liquid metal solutions in contact with a molten salt. The feasibility of the salt transport separation step was successfully demonstrated in two experiments with unirradiated materials. In the experiments, uranium in a molten Cu-Mg donor alloy (which also contained inactive fission product elements) was transferred incrementally to a molten Mg-35 w/o Zn acceptor alloy by cycling molten MgCl_2 between the two liquid alloys, which were in adjacent vessels. Satisfactory uranium transfers and fission product removals were achieved in these tests. A product wash step utilizing a Mg-20 w/o Zn alloy was effective in removing residual amounts of fission product elements that were transferred with the uranium.

The performance of equipment components in processes employing molten salt systems is being evaluated in an instrumented loop (constructed of type 304 stainless steel) in which molten chloride salt (MgCl_2 -30 m/o NaCl-20 m/o KCl) is circulated. One of the equipment items undergoing long-term testing is a centrifugal pump. During the time that the loop has been operated (a cumulative time of 160 hr), the pump has satisfactorily circulated the molten salt at 510 to 550°C at an average flow rate of 0.8 gpm, but flow rates up to 3.5 gpm were attained at impeller speeds well below the design limit. Other components of the loop, such as the freeze valve, flow meter, and inductance pressure tap, operated routinely. After 110 hr of loop operation, chemical analyses of the circulated salt showed (1) an increase in the chromium concentration from 0.001 w/o to 0.01 w/o, (2) a decrease in the oxygen content from 0.3 w/o to 0.1 w/o and (3) no detectable amounts of iron and nickel.

A materials testing program is being conducted to evaluate the suitability of various materials for ap-

plication in pyrochemical flowsheets employing liquid magnesium-base alloys in combination with molten chloride salts. Cast iron is being tested as a potential container material for Cu-Mg-U/halide salt systems. One cast iron crucible which was exposed to a Cu-9.7 w/o Mg-2 w/o U and MgCl_2 -30 w/o NaCl-20 w/o KCl system for 170 hr at 800°C and for 216 hr at 850°C showed no visual evidence of corrosion. However, metallographic examination revealed the formation of metal surface film, about 5 to 15 mils thick, which appeared to be primarily a Cu-Mg-U metal phase. A second cast iron crucible was exposed to a Cu-9.7 w/o Mg-2 w/o U and MgCl_2 system for 192 hr at 850°C with no visual evidence of serious corrosion. The stability of the solute uranium in cast iron containers was also examined. Although the results are not considered conclusive, it appears that Cu-Mg solutions of uranium in cast iron may be unstable. A uranium loss equivalent to about 0.02 g of uranium/cm² of crucible surface area was encountered. This uranium loss may be acceptable for some applications, especially if some of this loss can be recovered or if the loss can be diminished by repeated use of the same crucible. However, further work is needed before a complete assessment of this can be made.

The corrosion resistance testing of Croloy 16-1, a ferritic stainless steel, to Cu-Mg/halide salt systems was continued. Metal specimens in the form of agitator blades were exposed to a Cu-9.7 w/o Mg-2 w/o U and MgCl_2 -30 m/o NaCl-20 m/o KCl system for 197 hr at 800°C and to Cu-9.7 w/o Mg-2 w/o U and 100% MgCl_2 system for 191 hr at 850°C. The corrosion rates observed in the salt and vapor phases were approximately the same (~1 to 4 mils) in the two runs. In the run performed with MgCl_2 at 850°C, metal phase and metal-salt interface corrosion were much more severe in localized areas where depths of attack up to 100 mils and 50 mils, respectively, were encountered. Because the areas of severe localized corrosion were located on opposite sides at opposite ends of the blades, it is believed that fluid dynamics played an important role in the corrosion. The mechanical action of the fluid over the surface may have removed the surface reaction film that had formed and which may be normally protective. Croloy 16-1 was also subjected to a test in which a highly stressed specimen was contacted with MgCl_2 at 850°C for about 70 hr. No evidence of ordinary corrosive attack or of stress corrosion cracking was indicated.

Vitreous carbon was further tested as a container material. At 800°C, this material appears to be resistant to systems consisting of a halide salt and one of the following alloys: Zn-U, Zn-Mg-U, and Cu-Mg-U. In a test with a Zn-2 w/o U alloy, wetting of

the crucible surface exposed to the system increased from 10% after 417 hr to 50% after a total exposure time of 655 hr. In both instances, the wetting did not cause sticking of the charge. Exposure to a Cu-10 w/o Mg-2 w/o U alloy for 321 hr resulted in no wetting. These results indicate that vitreous carbon offers promise as an excellent container material for these systems.

In fabricating finished tungsten shapes by the pressing-and-sintering technique, the addition of about 0.1 w/o nickel to the tungsten is apparently useful in reducing the porosity of the finished piece. Further corrosion tests of this material were conducted. After exposure of agitator blades of nickel-impregnated tungsten to a Zn/ MgCl_2 -30 m/o NaCl-20 m/o KCl salt system at 800°C for 380 hr, no appreciable corrosion (<0.2 mil) or structure change during exposure was noted. Thus, the small nickel addition does not significantly affect the corrosion properties of tungsten in zinc/salt systems.

Pyrolytic boron nitride is another candidate material for process application. This material can be vapor-deposited in thin sections on graphite to provide a coating that is impervious to gases. A graphite crucible with a 2- to 5-mil coating of boron nitride did not show evidence of salt or metal leakage after testing in a Zn-5 w/o Mg-2 w/o U and MgCl_2 -30 m/o NaCl-20 m/o KCl system at 800°C for about 400 hr.

Recent advances in the quality and density of the available forms of graphite and silicon carbide have led to the reexamination of these materials for the containment of process solutions. Earlier tests had indicated that these two materials were porous to molten salts. Recent tests have been performed with high density forms of graphite and silicon carbide. Crucibles fabricated of three commercial grades of graphite (ATJ, CGW, and ZTA) have successfully contained a Zn-U/ MgCl_2 -30 m/o NaCl-20 m/o KCl system for approximately 100 hr at 800°C. Sectioning of the wall of the ATJ graphite crucible revealed no penetration of the salt phase. A crucible of high density silicon carbide successfully contained molten MgCl_2 for 24 hr at 800°C.

Alloys of aluminum-magnesium are potentially useful as solvents for use in the disposal of radioactive wastes containing fission product yttrium and rare earths. The corrosion resistance of four ferrous alloys (1020 carbon steel, type 4130 chrome steel, types 304 and 405 stainless steel) to 60-90 w/o Al-Mg/ MgCl_2 -30 m/o NaCl-20 m/o KCl systems was determined at 500°C and 800°C in 400-hr tests. In these tests, cerium (5 w/o) was added to the metal phase to represent the rare earths. Each metal coupon and its solvent medium was sealed in a tantalum capsule and

rotated end-over-end. The test results indicated that, in general, Al-Mg/salt systems are highly corrosive to ferrous alloys. At 800°C, all samples were completely destroyed in 400 hr. At 500°C, all samples except the type 304 stainless steel (<1 mil/400 hr) were severely corroded at aluminum concentrations below 90 w/o. It is concluded that ferrous alloys are not suitable container materials for Al-Mg/salt systems. Examination of the tantalum capsules showed that (1) at 500°C, very little corrosion (<0.5 mil/400 hr) occurred at any of the liquid metal compositions and (2) at 800°C, corrosion was observed and appeared to increase with increasing aluminum content of the metal phase (from 0.5 mil/400 hr at Al-40 w/o Mg to 3 mils/400 hr at Al-10 w/o Mg). At 800°C, many samples showed evidence of an intermetallic compound formation (possibly $TaAl_3$). These results suggest that tantalum also may not be a suitable containment material for extended service with Al-Mg alloys of high-aluminum content.

Tenelon steel, one of a relatively new class of steel alloys that is austenitic in structure (as is type 304 stainless steel), is being evaluated. These new materials possess excellent high temperature properties, good weldability, and relative ease of fabrication. When a Tenelon specimen was heated in air at 800°C for a total exposure time of 1000 hr, a protective oxide coating was produced (similar to that of the 18-8 stainless steels); such a coating causes the oxidation rate to decrease sharply with increasing exposure time. Thus, Tenelon should be usable in air at 800°C for periods of time well in excess of 1000 hr.

A shear-formed tungsten crucible fabricated by Metallwerk Plansee (Austria) is being tested for possible process application. After thermal cycling tests in argon for 15 cycles between 600 and 800°C showed no noticeable deterioration of the crucible, it was used as the container in salt transport separation experiments. In the first of these experiments, it was employed to contain a Zn-Mg-U/ $MgCl_2$ system at ~780°C; in subsequent experiments it was used to contain a Cu-Mg-U/ $MgCl_2$ system at ~850°C. Examination of the crucible after exposure to these two systems and to wash solutions for the uranium product for a total of about 130 hr showed it to be apparently in excellent condition. Testing of the crucible will be continued in future salt transport separation experiments.

Process Equipment Development—Skull Reclamation Process. After the fuel pins discharged from the EBR-II reactor are melt refined, a residue or skull containing uranium (about 5 to 10% of the melt refining charge) remains in the crucible. To recover

and purify this uranium, a skull reclamation process is being developed. This process consists of the following operations. The skull is first oxidized to a free flowing powder, after which the skull oxides are subjected to noble metal extraction, uranium oxide reduction, and uranium metal redissolution steps. The redissolved uranium is retorted to evaporate solvent metals (magnesium and zinc), and the resulting uranium sponge is melted. The recovered uranium is then returned to the melt refining process as makeup material.

Plant equipment for the process has been built and consists of three major equipment items: (1) a skull oxidation furnace, (2) a reduction furnace that utilizes a tungsten crucible and (3) a retorting furnace that utilizes a beryllia crucible. The latter two furnaces are sized for operation on about 5.8 kg of skull oxide (~5 kg of uranium oxide) and are being tested and remotely operated in a large argon-atmosphere enclosure (volume, ~4000 cu ft). The skull oxidation furnace is now in use in the EBR-II Fuel Cycle Facility.

The atmosphere in the large enclosure was recently returned to air to permit direct inspection of the reduction furnace; this furnace had been previously used for ten runs (see preceding semiannual report, ANL-7125, pp. 44–45). The interior of the tungsten crucible was found to be coated with about 2 kg of a rough cinderlike material which consisted principally of UO_2 , MgO , and ZnO . The crucible contained a metal heel (~700 g) composed of uranium, magnesium, and zinc. The Hastelloy C furnace body was in excellent condition; no corrosion was apparent and only traces of zinc and flux dust were found in the larger, upper section of the furnace body. The condition of the agitator assembly was good; no corrosion of the shaft or impeller was evident. Metal drive gears mounted on the mixer shaft and motor shaft showed considerable wear and were therefore replaced. The new gears, which were lubricated with APL¹ grease to which MoS_2 powder was added, showed no noticeable wear after eight additional runs described below. Prior to the start of a new series of reduction furnace runs, a second impeller was added to the mixer shaft and a three-bar vertical baffle assembly was installed in the tungsten crucible to improve mixing conditions within the furnace.

After the argon atmosphere was returned to the enclosure, eight runs with unirradiated material were performed in the reduction furnace using the flowsheet shown in Figure I-17. More vigorous reaction conditions (higher temperatures, longer contact times,

¹ Product of Shell Development Company, California.

and faster mixing) were employed in these runs than in the previous ones. The objectives of the recent runs were (1) to check the mechanical performance of the equipment, (2) to study the performance of three different MgCl_2 -based salt fluxes, and (3) to determine the effect of fluoride ion in the flux upon the removal of fission products and the reduction of uranium oxide.

The following general conclusions were drawn from the second series of runs. (1) Operation of the reduction furnace continued to be reliable and reproducible. (2) The three fluxes tested were nearly equivalent relative to uranium reducibility. (3) The presence of 10 m/o fluoride ion in the salt flux was beneficial to uranium reduction (reductions of 99% were achieved routinely). Fluoride ion in the salt did not appear to have a significant effect on ruthenium removal in the noble metal extraction step, but it appeared to inhibit molybdenum removal. Removals of fission product elements molybdenum, ruthenium, cerium, and zirconium were adequate for the EBR-II fuel cycle.

A uranium recovery of 92.6% in the product solution was typical of runs performed under favorable operating conditions. This recovery is equivalent to about 99% overall uranium recovery for the melt refining and skull reclamation processes. No further process testing in this equipment is planned.

In the final step of the skull reclamation process, the product uranium is recovered by retorting the Zn-Mg-U solution produced in the dissolution step. In the recent series of reduction furnace runs, the small amount of flux that is transferred with the U-Zn-Mg product from the reduction furnace was removed by pouring the molten product solution through a simple trap made of alumina-silica fiber. The flux, which preferentially wets the body of the trap, is retained. The use of the trap has eliminated contamination of product solutions by flux and subsequent difficulties with calcium ion and fluoride ion in the BeO retorting crucible. Nineteen runs were completed in the plant retorting unit located in the large argon-atmosphere enclosure. Four different thixotropically cast beryllia crucibles were used in the runs. All four crucibles are still intact. Although they adequately contained the bulk of the uranium product, a small quantity (estimated to be less than 25 g) of uranium was found, after each of the nineteen runs, in the annular space between the beryllia crucible and its graphite secondary container. This uranium loss is attributed to seepage of the retorting solution through the crucible wall. This problem, however, is not considered to be serious and should be overcome by improved crucible fabrication.

In each of the recent runs except one, the retorted

product ingot was dumped out of the beryllia crucible with ease. In the one run, moderate mechanical prying was required to free the ingot. As in previous runs, the retorting assembly contained the zinc-magnesium vapors effectively. Operation of the retorting assembly was satisfactory. The use of "bump" detecting devices combined with better control of power input to the furnace has proven effective as a means of eliminating the problems of unstable boiling conditions that were initially encountered in this recent series of retorting runs.

The skull reclamation process has been successfully demonstrated. The installation of the reduction furnace and retorting furnace in the Fuel Cycle Facility, however, has been postponed. The retorting furnace will be used at Argonne to test improved beryllia crucibles and investigate retorting operations in other pyrochemical processes.

Fuel Cycle Facility Operations. In the current reporting period, a total of 65 irradiated fuel assemblies from the EBR-II Reactor were processed in the Fuel Cycle Facility (FCF). When the fuel elements were examined after the subassembly dismantling step, no defective elements were found. Fabrication was also completed of 65 subassemblies utilizing fuel elements of the Mark IA design which permit greater burnup levels to be attained; the fuel elements were fabricated of reprocessed fuel and unirradiated fuel.

Among the irradiated fuel subassemblies that were being examined and processed was the first subassembly (C-162) which had been fabricated from irradiated fuel; this subassembly had been returned to the reactor and was reirradiated to a maximum burnup level of 1 a/o. Examination of various samplings of fuel elements from this subassembly showed no swelling of the cladding, no apparent change in the appearance of the element exterior surface, and no significant increase in the fuel pin diameter. When fuel growth data from this subassembly were compared with similar data from fuel assemblies that had been fabricated from unirradiated fuel and irradiated to about the same burnup level, the fuel growth was observed to be about the same.

Production of the Mark IA fuel pin was initiated. The new fuel pin is slightly shorter and more highly enriched than the Mark I pin. Because of the change in pin length, a slight change in the operation of the decanner portion of the decanner-pin processing machine was needed; in addition a new, modified shearing station was designed and built. As a result of the design changes, the working lifetime of the shear blades has been extended. The decanning and chopping functions were also separated. Their separation has resulted in improved operation. Improvements

have also been made in the bond tester which is used to detect discontinuities in the sodium bond and to indicate the height of the sodium above the upper end of the clad fuel pin.

Since the installation of equipment for the Skull Reclamation Process has been postponed, arrangements have been made to have the uranium in the melt refining skulls recovered by the Idaho Chemical Processing Plant (ICPP), Idaho. Currently, the skulls are being converted to an oxide form in the skull oxidation furnace located in the FCF. The oxidized skulls are then sent to the ICPP for storage and processing.

Because of the radioactivity of contaminated slave ends of the Model A manipulators in the FCF Air Cells, major overhauls carried out periodically are considered to be more economical than more frequent repairs of specific malfunctioning parts. Accordingly, the slave ends of all nine Model A manipulators in the Air Cell have been completely overhauled.

Absolute axial and radial burnup values have been experimentally determined for thirteen fuel subassemblies in the EBR-II reactor. The measured absolute values were in reasonably good agreement with those obtained from theoretical calculations.

Information has been obtained on the amounts of plutonium-239 and uranium-236 produced in fuel (core) subassemblies and of plutonium-239 formed in blanket subassemblies. These data are useful in determining burnup levels in the core and blanket materials.

II. Fluidization and Volatility Processes (pages 64 to 131)

Laboratory-scale Investigations. Fluorination studies are being carried out in a 2-in. dia. fluid-bed reactor to determine conditions for fluorinating $\text{UO}_2\text{-PuO}_2$ -fission product (F.P.) pellets that would result in a minimum retention of uranium and plutonium in a fluidized bed of alumina particles. Two fluorinating agents are being evaluated: fluorine and bromine pentafluoride. Fluorination of the pellets is carried out by a two-zone simultaneous oxidation-fluorination process or by a stepwise oxidation-fluorination method. The latter method has been used in all runs with BrF_5 , while both fluorination methods have been used with fluorine. A final fluorination step with 90 v/o fluorine (recycle-fluorination) is required in all cases to reduce the uranium and plutonium concentrations in the fluidized alumina bed to low levels.

Two types of pellets have been used in these studies:

(1) Type I pellets fabricated from solid solution $\text{UO}_2\text{-PuO}_2$ powder and fission product oxides and (2) Type II pellets fabricated from physically mixed UO_2 , PuO_2 , and fission product oxides. Cesium is not present in the pellets and hence cesium fluoride has been added to the alumina beds in some runs to simulate more closely the fission product mixture which would exist in the reprocessing of irradiated fuels. Recent experiments have shown that differences between Types I and II pellets do not have a significant effect on uranium and plutonium retention in the alumina bed, but that the addition of cesium fluoride leads to increased retention of both uranium and plutonium.

The effect of pellet-to-alumina-charge ratio on plutonium volatilization from the alumina bed was determined in three runs using pellet-to-alumina ratios of 0.3, 0.6, and 1.2. The reaction sequence consisted of two-zone oxidation-fluorination and single-zone fluorination at 450°C , followed by recycle-fluorination for 1 hr at 450°C , 3 hr at 500°C , and 8 hr at 550°C . Charges of 0.33, 0.65, and 1.32 kg $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets were used with 1100 g of alumina; cesium fluoride was added in proportion to the pellet charge (0.6 g CsF for 0.65 kg pellets). The final concentrations of uranium and plutonium in the fluidized alumina beds corresponded to volatilization of greater than 99.9% of the uranium and 92.5, 94.7, and 95.3% of the plutonium for pellet-to-alumina ratios of 0.3, 0.6, and 1.2, respectively. Thus, plutonium retention in the alumina bed did not increase in proportion to changes in the pellet charge and volatilization of plutonium from the alumina bed was improved by increasing the pellet-to-alumina charge ratio from 0.3 to 1.2.

A three-step reaction sequence consisting of (1) pellet oxidation at 450°C , (2) uranium fluorination at 300 and 350°C with less than 20 v/o fluorine, and (3) plutonium fluorination with 90 v/o fluorine from 350 to 550°C , has been developed; this sequence diminishes the effect of cesium fluoride on plutonium retention in the alumina bed. During uranium fluorination at 300 and 350°C , less than 10% of the plutonium charge was volatilized from the alumina bed and, after recycle-fluorination, the concentration of plutonium in the final alumina bed was 0.009 w/o in both runs, corresponding to volatilization of 96.4% of the plutonium in the pellet charge for a single use of the alumina bed. At the present time, stepwise oxidation and fluorination appears more promising than the two-zone oxidation-fluorination method for eventual process use with fluorine as fluorinating agent. With the stepwise reaction procedure, fluorination of most of the uranium can be carried out at a lower temperature than now appears feasible for two-zone oxidation-fluorination and this lower fluorination temperature apparently affects the

final plutonium concentration in the alumina bed. Fluorination at low temperatures by the two-zone oxidation-fluorination method would be impractical because of low pellet oxidation rates below 400°C.

The use of BrF_5 as a selective fluorinating agent in reprocessing $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets was demonstrated in a preliminary run using a 1-in. deep bed of fuel pellets. The reaction sequence consisted of (1) pellet oxidation at 450°C, (2) fluorination with 2 to 8 v/o BrF_5 at 400°C, and (3) recycle-fluorination with 90 v/o fluorine for 1 hr at 450°C, 3 hr at 500°C and 8 hr at 550°C. Analyses of samples from the soda lime traps used for disposal of UF_6 , unreacted BrF_5 , and bromine reaction product indicated that no plutonium was volatilized during the BrF_5 step. The concentration of both uranium and plutonium in the final alumina bed was 0.008 w/o; these results compared favorably with concentrations of 0.010 w/o (U and Pu) obtained in an equivalent run using the oxygen-fluorine cycle.

In five subsequent runs with BrF_5 , alternative recycle-fluorination schemes were investigated. In these runs, 2-in. beds of pellets (650 g) and 1100 g of alumina were used and the BrF_5 step was carried out at 300°C with approximately 10 v/o BrF_5 . Recycle-fluorination with 90 v/o fluorine for 5 hr of changing temperature from 300 to 550°C (10°C/12 min), following 5 hr of recycle-fluorination at 300°C, proved to be very effective in reducing the plutonium concentration to a low level of 0.006 w/o. Further, after the first hour of recycle-fluorination at 550°C, little plutonium volatilization was obtained during the subsequent 2 hr at 550°C and an additional 2 hr at 600°C. In another run, a shortened recycle fluorination sequence of 3 hr at 300°C, 5 hr from 300 to 550°C and 2 hr at 550°C was also effective and reduced the plutonium concentration in the final alumina bed to 0.007 w/o. During the 5-hr period of programmed temperature increase from 300 to 550°C, the rate of plutonium removal increased significantly between 350 to 400°C. An additional run was therefore completed with emphasis placed on recycle-fluorination at temperatures less than 450°C. The recycle-fluorination sequence consisted of 2 hr at 300°C, 3 hr at 350°C, 3 hr at 400°C, 2 hr at 450°C, 1 hr at 500°C, and 3 hr at 550°C. This sequence was also effective in reducing the plutonium concentration in the final alumina bed to 0.007 w/o; however, the increased time at temperatures less than 450°C during recycle-fluorination did not result in a decrease in plutonium retention.

The fluorination of oxidized $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets with BrF_5 was demonstrated at 200°C, and plutonium removal during recycle-fluorination, as the temperature was increased from 200 to 550°C, was investigated.

During 5.5 hr of fluorination at 200°C with 10 v/o BrF_5 , average production rates of 14 lb UF_6 /(hr) (sq ft) were maintained, compared with 40 to 45 lb UF_6 /(hr) (sq ft) obtained in the previous runs using 10 v/o BrF_5 at 300°C. The plutonium concentration in the final alumina bed was 0.009 w/o; therefore, in terms of plutonium retention in the final alumina bed, it appears that there may be no advantage in conducting the BrF_5 step at 200°C and the subsequent recycle-fluorination from 200 to 550°C, as compared with a BrF_5 step at 300°C followed by recycle-fluorination from 300 to 550°C.

Samples of bed material from experiments in a fluid-bed reactor and unused alumina were analyzed for surface area and particle size. Use of the alumina for a single run increased the surface area of the particles, as well as the amount of fine particles of less than 170 mesh size. The increase in surface area corresponded to what would be expected only from the formation of an aluminum fluoride film without other structural changes of the particles. The slight increase in the concentration of fine particles was that expected for attrition of an unreacted bed due to fluidization.

The surface concentration and distribution of plutonium and fission products on alumina bed material has been examined by several techniques including electron probe microanalysis. While no definitive conclusions regarding the mechanism of retention of plutonium on the surface of the alumina particles can be drawn, it has been shown that plutonium is located in a thin layer on the surface of the alumina particles and that plutonium is always found in this layer accompanied by fission products.

The study of the kinetics of the reaction of BrF_5 with various uranium compounds has been continued. Rate data are presented for the reactions between BrF_5 and UF_4 , UO_2F_2 , and U_3O_8 . Activation energies of 16.9, 8.3, and 9.2 kcal/mole were calculated for the reactions with UF_4 , UO_2F_2 , and U_3O_8 , respectively. The dependence of the rate constant on the partial pressure of the fluorinating gas was fractional, 0.38, for the $\text{UF}_4\text{-BrF}_5$ reaction; for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ and $\text{U}_3\text{O}_8\text{-BrF}_5$ reactions, the pressure dependence approached first order, 0.71 and 0.90, respectively. Experimental evidence indicates that bromine is the only bromine-bearing reaction product of the BrF_5 component of these reactions. The following equations represent the temperature and pressure dependence of the rate constant, k' (min^{-1}), for these reactions.

$$\text{UF}_4\text{-BrF}_5 (200\text{--}275^\circ\text{C}; 138\text{--}370 \text{ torr})$$

$$\log k' = 4.286 - 3690/T(^{\circ}\text{K}) + 0.38 \log P_{\text{BrF}_5} (\text{torr})$$

$\text{UO}_2\text{F}_2\text{-BrF}_5$ (175–300°C; 131–357 torr)

$$\log k' = -1810/T(^{\circ}\text{K}) + 0.71 \log P_{\text{BrF}_5} (\text{torr})$$

$\text{U}_3\text{O}_8\text{-BrF}_5$ (220–360°C; 89–369 torr)

$$\log k' = -0.220 - 2000/T(^{\circ}\text{K}) + 0.90 \log P_{\text{BrF}_5} (\text{torr}).$$

Condensed phase equilibria in the system $\text{MoF}_6\text{-UF}_6$ were studied by thermal analysis of hexafluoride mixtures varying in composition from 0 to 100 m/o UF_6 . The temperature-composition phase diagram constructed from the thermal arrests reflects the formation of solid solutions in the mixtures, a minimum melting mixture at 22 m/o UF_6 and 13.7°C, and a solid miscibility gap. The diagram indicates that the maximum solid solubility of MoF_6 (the smaller molecule) in the UF_6 lattice is about 30 m/o MoF_6 , while the maximum solid solubility of UF_6 in the MoF_6 lattice is 12 to 18 m/o UF_6 . This solid solubility relation is analogous to other binary systems in that the solubility of small atoms in a lattice of large ones is greater than the solubility of large atoms in a lattice of small ones.

The solid-state transformation of MoF_6 was observed to increase from approximately -10°C in pure MoF_6 to approximately -5°C in UF_6 mixtures. This behavior is the basis for a peritectoid in the phase diagram; it also indicates that the solid solubility of UF_6 is greater in the low-temperature form of MoF_6 than in the high-temperature form of MoF_6 .

X-ray diffraction patterns for the high-temperature form of MoF_6 can be indexed as a cubic structure, while the patterns for the low-temperature form of MoF_6 can be indexed as an orthorhombic structure, similar to, but not necessarily identical to, the orthorhombic structure of UF_6 . Since both UF_6 and the low-temperature form of MoF_6 have similar structures, it might be expected that the solid solubility of UF_6 would be greater in the low-temperature form of MoF_6 than in the high-temperature form.

The solid density of the high-temperature form of MoF_6 , determined from measurements of weight and volume, was 2.91 g/cc at 8°C and 2.88 g/cc at 0°C . The density calculated from X-ray diffraction patterns obtained at 10°C , assuming a body-centered cubic unit cell containing 14 atoms ($2 \times \text{MoF}_6$), was 2.88 g/cc. The agreement between this calculated value and that obtained from weight and volume measurements confirms the cubic structure for the high-temperature form of MoF_6 .

The melting-point diagram for the system $\text{UF}_6\text{-PuF}_6$ has been determined by applying the techniques of thermal analysis described above to mixtures with com-

positions covering the entire range 0 to 100 m/o. Owing to the extensive super cooling of the mixtures, and, presumably, to the small sample sizes (1 to 4 g), accurate measurements of the transition points were impossible to obtain from cooling curves. All measurements of solidus and liquidus points were therefore obtained from melting curves. All melting phenomena occurred between the melting temperatures of the pure components, and each mixture melted over a temperature interval. These observations indicated that solid-liquid equilibria in the $\text{UF}_6\text{-PuF}_6$ system involves a continuous series of solid solutions; the temperature-composition diagram is characteristic of such a series.

Observed liquidus points fell on both sides of the ideal liquidus curve, but all of the observed solidus points occurred at temperatures lower than the ideal solidus curve. This behavior might be the result of soluble impurities or a thermodynamic deviation from ideality, but it is quite likely the result of fractional crystallization during freezing preceding the determination of melting points, since the mixtures were not annealed in the solid state.

Two measurements of the melting point of pure PuF_6 by thermal analysis were 51.5 and 51.3°C . The best literature value is 51.59°C , obtained from the intersection of vapor pressure curves of solid and liquid phases.

An investigation is continuing to determine the rates of corrosion of nickel-200, nickel-201, Monel, Inconel, Duranickel-301, HyMu-80, INOR-8, nickel-200 weld, nickel-61 weld, and silver solder by fluorine, UF_6 and by some of the volatile fission product fluorides (namely, GeF_4 , AsF_5 , TeF_6 , SeF_6 , MoF_6 , BrF_5 , NbF_5 , and SbF_5) either individually or in the presence of fluorine. Data were obtained at 500°C for exposures up to 30.0 hr. Corrosion rates and measurements of intergranular penetration have been obtained. Of the metals examined, nickel-200 and Monel are the metals which exhibit the best overall resistance to corrosion by the volatile fission product fluorides individually and in the presence of fluorine at 500°C .

Engineering-scale Investigations. Engineering-scale development work is in progress on a fluid-bed fluoride volatility process for the recovery of uranium and plutonium from spent uranium dioxide fuels. The process scheme under current investigation includes the following basic steps: decladding, fluorination of the $\text{UO}_2\text{-PuO}_2$ fuel to the corresponding hexafluorides, distillation of $\text{UF}_6\text{-PuF}_6$ mixtures, and conversion of the mixed hexafluorides to dense particles of $\text{UO}_2\text{-PuO}_2$. In addition, thermal decomposition of PuF_6 is being studied as a means for separating the plutonium as solid PuF_4 from gaseous mixtures of PuF_6 and UF_6 . Process steps are to be demonstrated with nonirradiated ura-

nium-plutonium materials in three pilot-scale units—a fluorinator, a distillation column, and a converter—installed in an engineering-scale alpha facility. The thermal decomposition studies are being made in the converter. The facility comprises two large alpha boxes; the larger box contains the main process equipment, and the smaller box houses auxiliary equipment.

Experiments with plutonium-bearing materials were continued in the fluorinator and converter systems. The initial program for the fluorinator is aimed mainly at obtaining information on the behavior of plutonium in engineering-scale equipment. The first campaign consisted of three successive experiments on equal-sized batches of material. These experiments are being followed by a cleanup fluorination experiment to recover plutonium deposited in process equipment and lines as a result of thermal or alpha decomposition, or chemical reaction.

In each of the second and third fluorination experiments, the charge consisted of ~ 8.8 -kg batches (~ 12 -in. depth) of nominal 0.5 w/o $\text{PuO}_2\text{-UO}_2$ pellets (containing inactive fission product oxides) and about 7 kg of Alcoa Tabular T-61 alumina, of a nominal 48 to 100 mesh size. In these tests, the starting alumina bed was the final bed from the previous experiment. The alumina bed extended about 2 ft above the pellet bed. Fresh alumina was added to the bed to replace that removed by sampling.

The run sequence consisted of a two-zone oxidation-fluorination period, in which the bulk of the uranium was converted to UF_6 , a one-zone fluorination reaction period, and finally a cleanup period characterized by total gas recycle, high fluorine concentrations (to 90 v/o), and higher temperatures (to 550°C) than that (450°C) used in the two preceding periods. During the two-zone period, oxygen concentrations to 25 v/o (in nitrogen) were used to effect the oxidative pulverization of the fuel pellets, and the concentration of fluorine fed to the zone above the pellets was ~ 10 v/o.

The cleanup fluorination experiment, now in progress, is being conducted in two parts: the first part, already completed, consisted of exposure of the bed to an additional 21 hr of fluorine (6 hr in the temperature range 350 to 550°C , and 15 hr at 550°C). The second part of the cleanup fluorination involves exposure of all equipment components including valves, cold traps, and product receivers to fluorine at temperatures near 300°C . This work is now in progress.

Results show that plutonium and uranium retention in alumina with successive reuse of the bed does not increase directly with the number of charges processed; at the end of the first fluorination run, the plutonium and uranium concentrations in the alumina were each

~ 0.02 w/o. After three batches of fuel were processed and after the cleanup fluorination experiment, final grab samples taken with the bed fluidized showed a plutonium concentration of 0.04 w/o and a uranium concentration of 0.03 w/o. These values correspond to overall removals of $\sim 97\%$ and 99.9% , respectively. Considering the fact that this was the first series of experiments, the results obtained are very encouraging. A final sample taken from the bed after its withdrawal from the reactor showed a slightly higher plutonium content, ~ 0.06 w/o. A fraction of the bed (fines which are relatively high in plutonium content), which is apparently retained in upper portions of the reactor (filter zone), returns to the bed after the run when fluidization ceases, and contaminates the bed material. Revised operating procedures, such as intermittent reductions in gas flow and the raising of filter zone temperatures to near 300°C for several hours at the end of a given experiment, are suggested to allow more complete cleanup of the system. Material balance data will become available upon completion of the equipment cleanup fluorination test.

The exploratory program for the study of thermal decomposition of PuF_6 in a fluid-bed system was successfully completed. In the thermal decomposition process, a mixture of $\text{UF}_6\text{-PuF}_6$ is passed through a fluidized bed at about 300°C and ideally the plutonium deposits on the surface of the bed particles as solid PuF_4 . Two experiments were conducted at 300°C using a 2-kg bed of -100 mesh Alcoa, Tabular T-61 alumina as a stand-in for the conceptual bed of PuF_4 . The final bed from the first run was used as the starting bed for the second run. In each experiment, approximately 10 kg of a $\text{PuF}_6\text{-UF}_6$ mixture, diluted to 40 v/o hexafluoride with nitrogen, was processed in about 8 hr.

The decomposition process at this temperature appears quite efficient, as indicated by the low plutonium content of both the UF_6 off-gas stream (from grab vapor samples) and the final collected batches of UF_6 (liquid hexafluoride samples). The average plutonium value for a series of seven grab samples of vapor, taken at approximately hourly intervals during the final experiment, was 0.0004 w/o plutonium. Using the final bed analysis for plutonium, 1.46 w/o, as a basis for the feed plutonium concentration, a separation factor of about 99.9% was calculated. The final uranium content of the bed was low (0.19 w/o) after the two successive experiments. It was observed that deposition of PuF_6 as solid PuF_4 occurred preferentially on the surface of the bed particles rather than in the gas phase, producing a solid product that was relatively easy to transport. Although material balance results are not complete, feasibility of a fluid-bed concept for thermal

decomposition appears likely. Further work in this fluid-bed reactor (converter) is being directed toward the preparation of dense mixed $\text{PuO}_2\text{-UO}_2$ particles by the direct reaction of $\text{PuF}_6\text{-UF}_6$ mixtures with steam and hydrogen.

Preliminary testing of the distillation column, erected in a mock-up area, is continuing. Results of boil-up checks with Freon-113 as a stand-in for the hexafluoride, and overall performance of the distillation system components, including adiabatic operation, were all satisfactory. The work remaining to be done while the distillation column is in the mock-up area centers mainly on calibration of flowmeters with UF_6 . The unit will be installed in the large alpha box upon completion of these tests.

Process development work on decladding Zircaloy-clad low-enriched uranium dioxide fuel bundles by reaction of the cladding with HCl was continued in a pilot-scale fluid-bed reactor facility. A fuel bundle, 70 in. long, comprising four Zircaloy tubes packed with UO_2 pellets and two Zircaloy rods, was contacted with 48 to 64 v/o HCl in a 12-in. deep fluid bed at fluidizing-gas velocities of ~ 0.5 ft/sec, and at a fluid-bed temperature of $\sim 400^\circ\text{C}$. The halogenation reactor and its auxiliaries performed satisfactorily during the entire period (4.5 hr) of decladding.

Inspection of a Zircaloy rod, taken out of the reactor after partial hydrochlorination, indicated that the portion of the rod in the fluid bed was free of any coating and that the penetration rates were about 16 mils/hr, whereas the portion of the rod above the fluid bed was coated with a gray friable layer and the penetration rates ranged from 6 to 9 mils/hr. Penetration rates up to 75 mils/hr were observed on the portion of the rod located above the fluid bed in the zone where the diameter of the reactor increases from 6 in. to 12.5 in. Temperatures of the second Zircaloy rod, measured with skin thermocouples spot-welded 6 in. apart along its entire length, indicated that in the fluid-bed zone the temperatures of the rod were similar to those of the fluidized bed, thereby indicating that heat transfer from the rod to the fluidized bed was good. In the gas phase above the fluid bed, the temperature of the rod was much higher, up to 640°C , although the temperatures of the surrounding gas phase and the reactor wall were 400°C thus indicating that the heat transfer from the rod to the surroundings was poor. These data on penetration rates and temperatures indicate that it probably is possible to declad long fuel bundles in shallow fluidized beds; however, experiments with larger tube bundles in larger reactors are needed to establish this point firmly.

The use of BrF_5 as a selective fluorinating agent for uranium in fluidized beds of alumina is being investi-

gated as an alternative method for processing declad UO_2 fuels, using a bench-scale reactor ($1\frac{1}{2}$ -in. dia.) system. UO_2 pellets were oxidized to U_3O_8 fines and the fines were contacted with bromine pentafluoride at several concentration levels (30 to 49 v/o in nitrogen) in one series of tests and at various bed temperatures (110 to 385°C) in another series of tests. Fluorination rates increased with an increase in concentration of BrF_5 and with increased temperature of the fluid bed. Concentrations in excess of 10 v/o and temperatures over 200°C appeared to produce practicable fluorination rates.

Studies were made in an engineering-scale fluid-bed reactor (3-in. dia.) system to determine whether samples of the fluid-bed material taken after oxidation of the UO_2 fuel are representative of the fuel charge. In these experiments, 2.2 to 4.4 kg of fragmented UO_2 pellets, containing a mixture of depleted (0.2198% ^{235}U) and normal (0.7218% ^{235}U) UO_2 pellets, were oxidized in beds of alumina with 20 v/o oxygen in nitrogen at $\sim 450^\circ\text{C}$ for periods of 5.5 to 11 hr. The resultant beds contained large quantities (40 w/o) of U_3O_8 fines. It was found from analyses of fluid-bed samples that after 5.5 hr of oxidation, the ratios of ^{235}U to ^{238}U in the fluidized bed approached equilibrium values, which were uniform throughout the fluid bed. These results suggest that fluid beds containing large quantities of uranium fines can be representatively sampled for accountability purposes.

Fluorination of the U_3O_8 fines was carried out as follows: during the period when large quantities of fines were present, the system was contacted with 6 to 12 v/o fluorine at 350°C with fluidizing-gas velocities of 0.9 to 1.5 ft/sec. As the quantity of fines decreased, the concentration of fluorine was increased to ~ 95 v/o, the gas velocity was decreased to ~ 0.2 ft/sec, and the temperature was increased to $\sim 500^\circ\text{C}$. Uranium hexafluoride production rates averaged about 50 lb/(hr) (sq ft) when large quantities of fines were present. In view of the successful development of processing the declad UO_2 by the two-step oxidation-fluorination procedure, the engineering-scale equipment is being modified to accommodate BrF_5 as the fluorinating agent for the U_3O_8 fines.

A program for studying the fluid-bed processing of irradiated fuel materials is in progress. Experiments are being conducted in a $1\frac{1}{2}$ -in. dia. reactor installed in the senior cave facility. Preliminary results from four experiments with irradiated oxide fuels are presented in this report. The significant results are:

1. For two experiments with irradiated UO_2 , in which the fuel was first contacted with a gaseous mixture of HF and oxygen and then contacted with fluorine to volatilize the uranium, the decontamination factors

from beta and gamma activities were about 20. When a 400°C NaF pellet bed was interposed between the reactor and the uranium product trap, a decontamination of about 70 from beta and gamma activities was achieved. Considerably more ruthenium activity was shown to volatilize during the fluorination step than was experienced during fluorination of metal alloy fuels (see ANL-7125, pp. 98-103) suggesting a significant difference in the chemistry of ruthenium in these two systems.

2. Experiments with alternating irradiated and non-irradiated charges showed that residual levels of activity in the equipment can result in sample contamination in a run with irradiated material even when there is an interposing run with nonirradiated material.

3. One run with an irradiated $\text{UO}_2\text{-PuO}_2$ charge followed a similar run with a nonirradiated $\text{UO}_2\text{-PuO}_2$ charge made from the same batch of oxide. The results of these runs showed that irradiation had the apparent effect of increasing plutonium retention in the reactor bed material from 0.002 w/o (nonirradiated) to 0.007 w/o (irradiated). These residual plutonium values are similar to those obtained in bench-scale experiments with nonirradiated fuel containing added fission product elements, and tend to confirm the validity of the bench-scale results.

4. Considerable ruthenium movement throughout the process equipment was observed during the long-term fluorination of an irradiated $\text{UO}_2\text{-PuO}_2$ charge. Ruthenium retention was exhibited by nickel balls at 150°C, NaF pellet beds at 150°C and 400°C, a cold trap at -78°C, and activated alumina. These traps, operated in series during the fluorination step, were not sufficient to prevent a small but biologically significant fraction of the ^{106}Ru from appearing in the process off-gas. A series of tests were performed using additional sorbent materials. A significant decrease in the off-gas content of ^{106}Ru was achieved when the NaF pellets in the 400°C bed were replaced with a fresh charge of pellets. The run was completed without exceeding, on the average, the recommended upper limit for ^{106}Ru concentration in the air discharged from the cave to the environment. A stack gas sampling test was conducted which indicated that the ruthenium activity present in the stack gas was primarily gaseous.

The safe, economical disposal of gaseous reagents such as fluorine and other fluorinating agents is an extremely important consideration for the fluoride volatility reprocessing of nuclear reactor fuels. Since the gaseous reagents may be contaminated with volatile fission product compounds, the disposal system should produce a solid material convenient for ultimate waste disposal.

Bench-scale studies have been made to evaluate the disposal of fluorine using fluidized beds of activated alumina. This technique utilizes the excellent heat-transfer properties of a fluidized bed for control of the temperature of the highly exothermic reaction, thus preventing sintering of the alumina which has often occurred in packed-bed reactors.

Fluid-bed experiments show an excellent efficiency (over 99.9%) of fluorine removal with activated alumina and a capacity of activated alumina as high as 0.7 g F_2/g activated alumina. A factorially designed experiment has been planned to determine the effects of temperature, fluorine concentration, gas flow rate, bed particle size, and bed height on the disposal efficiency and on the capacity of activated alumina.

Basic Studies of Fluidized-bed Behavior. An experimental and theoretical investigation has begun to determine and predict the effect of reactor vessel walls on particle movement in fluidized beds. Knowledge of particle behavior would allow accurate estimation of heat and mass transport processes in fluid-bed systems and would facilitate the design of these reactors. An apparatus has been constructed to determine the residence times of particles at the walls and the heat transfer coefficients from the walls to the fluid bed, under similar conditions, in an attempt to relate the particle residence times to the heat transfer coefficients. It is expected that this work will result in an accurate and generalized correlation for prediction of heat transfer coefficients at the walls of vessels containing fluidized beds.

III. Materials Chemistry and Thermodynamics (pages 132 to 163)

High Temperature Materials Development. This program is directed toward the development of nuclear reactor materials that will be subjected to high temperatures (1500 to 3000°C). Its objective is to collect basic data on the vaporization and chemical stability of potential fuels, i.e., the oxides, carbides, nitrides, phosphides, sulfides, and arsenides of uranium, plutonium, and thorium, and their solid solutions; and on the reactions of these materials with other substances. The collected data will be useful for guidance in materials selection; it will also serve to advance knowledge of nonstoichiometry in solids, an important high-temperature phenomenon. Experimentation is carried out quantitatively so as to yield thermodynamic and phase-diagram information. Various complementary methods of investigation are used, according to the requirements of the particular problem.

During the past year, emphasis was placed on deter-

minations of the phase diagram of the condensed uranium-urania system, the equilibria between the vapor and condensed phases of this system, and the oxidation-reduction equilibria of urania. The specific objective of these studies was to obtain comprehensive thermodynamic data for compositions ranging from nearly pure uranium to slightly hyperstoichiometric urania. Progress in the general research program is reported below.

Final evaluation of our phase-diagram data for the uranium-urania system is being made and a manuscript covering this study is being prepared for journal publication. The experiments performed during the current report were directed toward clarification of questions arising from this evaluation. Minor refinements in the phase diagram previously presented were achieved. The composition of the monotectic was refined from 1.30 ± 0.10 to 1.33 ± 0.03 O/U atom ratio units, and the hypostoichiometric urania phase boundary was tentatively extended down to 1350°C .

An exploratory study of the uranium-urania-tungsten system was carried out. No unusual features were found, and the study was discontinued.

The experimental facilities for high-temperature phase-diagram studies have been expanded by the development of a thermal analysis apparatus. Initial testing indicates that the apparatus, though yet incomplete, is functioning with a very satisfactory sensitivity up to 2700°C .

The mass-spectrometric effusion studies of the condensed two-phase uranium-urania system have been completed. Good agreement with work previously reported was obtained. The following enthalpies of volatilization in the temperature range 1725 to 2125°C were derived (in kcal/mole): $\Delta H(\text{U}) = 117.2 \pm 1.4$, $\Delta H(\text{UO}) = 122.9 \pm 1.4$, $\Delta H(\text{UO}_2) = 138.0 \pm 1.4$.

The mass spectrometer was used to test the new experimental principle (proposed in an earlier report) whereby the composition of a solid is deduced from a continuous determination of the composition of the vapor above it. The evaluation of the continuously changing relative partial pressures of the UO and UO_2 species vaporizing from urania at about 2100°C yielded a reasonable evaluation of the changing composition of urania. The precision of the method was found to be limited by temperature fluctuations.

The composition of congruently vaporizing urania in the range 2000 to 2300°C has been determined by Knudsen effusion measurements. The O/U atom ratio varies from about 1.998 to 1.940 over this temperature interval.

The transpiration-equilibration method has been used to make an extensive set of measurements on urania of various compositions in the temperature

range 1800 to 2450°C . The oxygen partial pressures were observed to increase rapidly as the oxygen content of the solid phase increased, particularly near the stoichiometric composition, UO_2 . The total pressures of uranium-bearing species were found to go through minima (corresponding to compositions of congruent vaporization) at oxygen contents of the solid phase near, but below, the stoichiometric composition. Manuscripts covering this work are being prepared for journal publication.

Preparation of Reactor Materials—Ceramic Fuels. The synthesis of uranium-plutonium monocarbide is being studied in order to develop preparation procedures which economically fit into appropriate fuel cycles, and to make well-defined fuels for further experimental studies, particularly irradiation studies. A fluidized-bed process is being developed in which uranium or uranium-plutonium alloy is hydrided and then reacted with methane-hydrogen gas mixtures to form UC or $(\text{U,Pu})\text{C}$. By controlling the methane concentration in the fluidizing gas, formation of higher carbides can be prevented. Thermobalance experiments were carried out to determine the methane-hydrogen gas mixture that is in equilibrium with $(\text{U}, 20 \text{ w/o Pu})\text{C}$ and $(\text{U}, 20 \text{ w/o Pu})_2\text{C}_3$. The results indicated that the free energy change for the reaction $\text{C} + 2 (\text{U}, 20 \text{ w/o Pu})\text{C} \rightleftharpoons (\text{U}, 20 \text{ w/o Pu})_2\text{C}_3$ at 770 to 810°C was about -4 kcal/mole of $(\text{U}, 20 \text{ w/o Pu})_2\text{C}_3$.

Fluidized-bed experiments to produce UC and $(\text{U,Pu})\text{C}$ on a 300-g scale are being carried out in a $1\frac{5}{8}\text{-in.}$ ID reactor. Three runs have been conducted to prepare $(\text{U}, 15 \text{ w/o Pu})\text{C}$, under the following carburizing conditions: gas concentration, $10 \text{ v/o CH}_4\text{-}90 \text{ v/o H}_2$; total pressure, 4 atm ; bed temperature, 750°C ; run duration, 10 hr (except for first run). The product from the first run, which was terminated after 6 hr of carburizing was hypostoichiometric in carbon content (4.11 w/o), whereas the other two products (4.96 and 4.89 w/o carbon) were close to the stoichiometric composition (4.80 w/o carbon). The levels of oxygen impurity in the products of these runs were very low, averaging about 500 ppm or 0.05 w/o .

In runs that preceded the $(\text{U,Pu})\text{C}$ preparations, stoichiometric UC was produced in this same reactor in 6 to 8 hr of carburizing at 750°C . However, the oxygen content of samples of the product was 0.2 to 0.3 w/o . It is suspected that the oxygen was introduced during handling and sampling of the products. The UC products, which are more finely divided than the $(\text{U,Pu})\text{C}$ products, apparently react with atmospheric impurities more readily. Such oxidation evidently takes place despite the fact that the helium glovebox atmosphere contains only 6 to 7 ppm oxygen and 1 to 2 ppm water. The addition of a combination binder and oxidation

inhibitor to the UC powder prior to exposure to the glovebox atmosphere may alleviate this problem.

Engineering studies with a semiworks-scale (2-kg capacity) fluidized-bed reactor have demonstrated the feasibility of removing the UC product by pneumatically conveying it through a stationary tube extending to the bottom of the reactor. However, because the UC particles were very fine and were not always free-flowing, transfer of the product was sometimes difficult. The (U,Pu)C particles, which are larger in size, appear to be more easily fluidized, and, therefore, would be more easily removed from a reactor by pneumatic conveying. The semiworks-scale equipment, which is designed for operation at 10 atm and 850°C, has been recently modified to allow recirculation of the fluidizing gas.

A clear plastic column, of the same design as the semiworks reactor and the reactor in which (U,Pu)C is being prepared, has been used to confirm design theories for these reactors. Fluidization tests were conducted at room temperature in an air atmosphere using partially oxidized UC. Introduction of the fluidizing gas through a tube running down the axis of the reactor and discharging at the conical bottom afforded adequate fluidization in this model. Product withdrawal by pneumatic conveying through a tube was also demonstrated successfully.

Calorimetry. The standard enthalpy of formation, ΔH_f° , of boric oxide was determined by fluorine bomb calorimetry because of the uncertainty in this value as determined by previous investigators using solution calorimetry. Measurements were made on both crystalline boric oxide (the standard state) and amorphous boric oxide (the more common form), yielding the values $\Delta H_f^\circ_{298}(\text{B}_2\text{O}_3, \text{c}) = -303.0 \pm 0.4$ and $\Delta H_f^\circ_{298}(\text{B}_2\text{O}_3, \text{amorph.}) = -299.5 \pm 0.5$.

A previous determination at this laboratory of the enthalpy of formation of $\text{MoF}_6(\text{g})$ by fluorine bomb calorimetry showed that the literature value, based on hydrolysis of MoF_6 , was 10 kcal mol⁻¹ too negative. This discrepancy led us to suspect the literature value for the enthalpy of formation of $\text{WF}_6(\text{g})$, which is also based on hydrolysis. The value for $\Delta H_f^\circ_{298}(\text{WF}_6, \text{g})$ was determined directly by combustion of tungsten in fluorine and found to be -411.5 ± 0.4 kcal mol⁻¹, or 5 kcal mol⁻¹ less negative than the value based on hydrolysis.

The standard enthalpy of formation of phosphorus pentafluoride, $\Delta H_f^\circ_{298}$, was determined to be -380.8 ± 0.3 kcal mol⁻¹ by combustion of white phosphorus in fluorine. Other modifications of phosphorus—amorphous red I, crystalline red IV, and crystalline red V—were also burned in fluorine in an attempt to measure the standard enthalpies of transition. The

results obtained were (in kcal g-atom⁻¹): P(α -white) $\rightarrow$ P(amorph. red I), $\Delta H_{tr}^\circ = -3.9 \pm 0.2$; P(α -white) $\rightarrow$ P(red V), $\Delta H_{tr}^\circ = -3.9 \pm 1.0$; P(red IV) $\rightarrow$ P(red V), $\Delta H_{tr}^\circ = -1.2 \pm 1.0$.

A direct determination of the enthalpy of formation of carbon tetrafluoride (tetrafluoromethane) by fluorine bomb calorimetry has been undertaken. High-purity samples of natural and pyrolytic graphite have been prepared. Because graphite absorbs fluorine spontaneously in a nonreproducible manner, a two-chambered combustion bomb is being used to isolate the sample from fluorine prior to ignition. The two-chambered bomb was newly constructed for this study and is capable of charging the combustion chamber with fluorine to higher pressures than possible with the older model.

The graphite combustions will be the first fluorine combustions in which a Dymec quartz-crystal thermometer and automatic printout of time-temperature data are used.

Because of the great need for thermochemical data on plutonium compounds, this laboratory is planning to explore various experimental methods for their determination. The methods to be investigated include bomb and flow calorimetry using various oxidants (oxygen, fluorine, chlorine), solution calorimetry, and other types of reaction calorimetry. When methods and techniques appropriate to plutonium are developed, a program of calorimetric measurements on plutonium compounds will be initiated.

Fluorinating agents other than fluorine are being investigated to augment the technique of fluorine reaction calorimetry. The gases NF_3 and PF_3 show promise. Although chemically stable, NF_3 can function as a fluorinating agent. On the other hand, PF_3 is quite unstable with respect to PF_5 and can be used to strip fluorine from compounds.

A fluorine flow calorimetric system has been completely assembled and is undergoing testing. Although constructed primarily for the combustion of uranium compounds, the system can also be used with other substances that require careful control of fluorine flowrate during the reaction period. The system can be easily modified to accommodate gaseous reactants such as NF_3 and PF_3 .

Data have been obtained with the 1500°C drop calorimeter for the enthalpy, relative to 25°C, of samples of aluminum oxide and uranium monophosphide. However, there still exists some uncertainty about the optimum manner in which to treat the data. A provisional value for the mean heat capacity of uranium monophosphide between 800 and 1200°C is 13.8 cal deg⁻¹ mol⁻¹. Considerable experience in (satisfactory) operation of the calorimeter has been gained, and

marked improvement in the accuracy and precision of future measurements is expected.

The calorimetric system for determining enthalpy increments to 2500°C is being tested with all components assembled except for the copper-block calorimeter, optical viewing port, and water-cooled shutter. Shop work is complete on copper-block calorimeter II, and is progressing satisfactorily on the optical viewing port and water-cooled shutter.

Liquid Sodium Coolant Chemistry. The nature of carbon-bearing impurities in liquid sodium is being investigated because of their possible involvement in corrosion phenomena and, hence, in the use of sodium as a heat transfer fluid in nuclear reactors. Efforts are being directed toward the characterization, study of the reactions, and removal of such impurities. Further support of the hypothesis, that the major portion of the carbon found in reactor-grade sodium is particulate, was obtained by centrifugation experiments. Centrifugation of a liquid 56 w/o Na-44 w/o K alloy at 30,000 or 130,000 g resulted in reduction of the carbon content of its top layer from ~52 to ~28 ppm.

The tendency of particulate carbon in sodium to segregate was demonstrated by repeated, unidirectional, fractional melting of a column of sodium sealed in a fused silica tube. Sodium cores extruded from the middle and bottom sections of the tube were found to contain 3 to 4 ppm carbon, whereas the sodium residues adhering to the tube walls were found to be about 5 to 10 times more concentrated in carbon.

It has been shown that reactor-grade sodium does not contain significant (>1 ppm) amounts of stable, sodium hydroxide-soluble, aromatic compounds such as hexasodium hexacarbonyl, a reaction product of sodium with carbon monoxide.

An investigation of the stability and solubility of sodium cyanide in liquid sodium is under way. Preliminary results indicate that sodium cyanide is stable at elevated temperatures, both in the presence and absence of sodium, and that its solubility is very low, less than 100 ppm between 180 and 530°C.

The attempted preparation of carbon-free sodium by direct electrolysis of molten salt mixtures has been suspended because of difficulties encountered in scaling down the commercial process.

Chemistry of Liquid Metals. The chemistry of liquid metals and alloys is being investigated to provide basic data for the development and testing of theories of the metallic liquid state. The following experimental studies are part of the overall program.

Thermodynamic activities of alkali metals in their binary liquid solutions are being measured by atomic absorption spectrophotometry. In the course of these measurements, the partial pressure of monatomic

potassium over liquid potassium was determined at about 70°C. The measured pressures agree with literature values after taking into account such factors as (a) Doppler broadening and nuclear hyperfine splitting of the 7665 Å potassium resonance line, and (b) the emission line width of the hollow cathode lamp.

Evidence is being sought for the existence or non-existence of distinct atomic complexes in liquid alloys. For this purpose, an apparatus has been built to measure the velocity and absorption of high-frequency sound (pulse-echo method) in liquid metals. The velocities of sound in distilled water and mercury at room temperature were measured to test the reliability of the apparatus; the results were in excellent agreement with literature values.

The vapor over a 75 a/o potassium amalgam heated at about 200°C was examined by means of a Bendix TOF mass spectrometer. The only gaseous species detected were K, K₂, and Hg. The gaseous species HgK₃ and K₃, which had been postulated to exist in order to explain the vapor pressure behavior of potassium amalgams, do not exist or, at most, are very minor components of the vapor.

Metal-metal interactions, both in the liquid and solid states, are affected by small variations in atomic radius ratio. To study this effect, a systematic X-ray examination was made of the binary zinc-rich phases formed between the rare earths (lanthanons) and zinc. The influence of atomic size on structure and stoichiometry can be seen by listing the phases according to the size of the hole provided for the central lanthanon atom and by subdividing into groups according to structure type and coordination number. As expected, phases with higher coordination numbers provide larger holes for the central atom, and within each group the order parallels the lanthanide contraction.

IV. Reactor Safety (pages 164 to 213)

Metal-Water Reactions. The experimental program to determine rates and extents of reaction of molten fuel and cladding metals with water is continuing. In general, it has been necessary to study the reaction of each metal of interest by several methods. A high-pressure furnace, which was designed especially for isothermal studies of the reaction of steam with molten stainless steel and aluminum, has been used for experiments designed to simulate the environment of the fuel of a water-cooled power reactor following a loss-of-coolant accident. Previous studies of the reaction of single Zircaloy-2-clad and type 304 stainless steel-clad, UO₂-core simulated fuel elements (8-in. long

rods) with high temperature steam have been extended to include bundles of four such rods. The extent of reaction of a 4-rod bundle with type 304 stainless steel cladding was approximately the same as that of single rods reacted under identical conditions. The extent of reaction of a 4-rod bundle with Zircaloy-2 cladding was about twice that observed in single-rod experiments under identical conditions. The increased extent of reaction is attributed to self-heating, which was not observed in the runs with single rods. (The hot end of the bundle was more than 200°C above the furnace temperature.)

The Division of Reactor Development and Technology, U. S. Atomic Energy Commission, requested that a study be made to evaluate the possibilities of conducting large scale loss-of-coolant simulations by both laboratory and in-pile techniques. During the past half-year, a considerable effort was made to obtain the requested information. The objectives of the experiments under consideration would be to (1) test existing calculational models and (2) obtain the information necessary to continue the development of calculational models so as to describe the disassembly of the core of a reactor as cladding, cladding oxide, and fuel melting temperatures are reached. These evaluations, which also included preliminary cost estimates and schedules, were submitted to the Division of Reactor Development and Technology, USAEC for their consideration.

The calculational study to demonstrate the application of metal-water reaction data to the analysis of a loss-of-coolant accident in a reactor was continued. Previous analyses were made for the Loss of Fluid Test (LOFT) reactor. These analyses made use of a simple model to calculate the temperature and extent of cladding-steam reaction throughout the core following loss of coolant. The calculations performed for these analyses made use of many simplifying assumptions and ignored heat losses; however, they did predict the general features of such an accident and pointed out several gaps in the knowledge required for a precise analysis. A new computer program (CHEMLOC) has been written that takes into account the heat losses from the core and makes use of mass transfer calculations to describe the cladding-steam reaction with limited steam availability. Heat and mass transfer coefficients were determined analytically for the case of laminar flow of a fluid through a parallel array of rods. Also considered in the present calculations were entrance effects and the presence of spacers.

One of the experimental techniques used to study metal-water reactions made use of the energy from a pulsed ruby laser to heat small single particles of metal

in water. The previously reported experimental results of aluminum-water reaction studies carried out by this technique were used to develop a model that seems to satisfactorily describe the reaction of small aluminum particles in water. In this model a simple heat balance between rates of heat generation and loss is set up and solutions found for steady state temperature and reaction rate. The rate of reaction is considered to be controlled by the rate of diffusion of water through a hydrogen film surrounding the particle, and both convective and radiative heat losses are included. The effects of water pressure, added inert gas, and emissivity are also discussed in terms of this model. The observed experimental threshold of reaction has been identified with melting of a protective aluminum oxide coating surrounding the metal particle.

Another general method of studying metal-water reactions involves nuclear heating of typical reactor fuel materials submerged in water. A series of eighteen photographic experiments was carried out in the Transient Reactor Test (TREAT) facility to obtain additional information on the in-pile behavior of aluminum-clad fuel materials. In these experiments, high-speed color motion pictures were taken of small samples of aluminum-clad fuel submerged in 30°C water during their exposure to transient bursts of neutrons in TREAT. Two types of fuel samples were used in these experiments. The first, Spert 1-D fuel, was a fully enriched 23 w/o uranium-aluminum alloy 0.020-in. thick, clad with 0.020-in. thick 6061 aluminum. The second, HFIR fuel, was fully enriched 41.45 w/o U_3O_8 -aluminum cermet, 0.030-in. thick and clad with 0.010-in. thick 6061 aluminum. The samples were cut from plates to a size of 0.5 by 1.5 in. The two fuel types showed qualitatively similar behavior in the extents of metal-water reaction observed. In each case, no significant reaction was noted until a threshold fission energy input was reached; from this point on, the extent of reaction increased fairly rapidly with increasing energy input.

As a result of these photographic studies plus the earlier nonphotographic TREAT studies, the following qualitative description of the aluminum-water reaction in the TREAT experiments now seems evident.

- 1) Below temperatures of 1750°C, the reaction of aluminum is characterized by the formation of a protective oxide and the evolution of hydrogen bubbles. The samples rapidly quench after the nuclear burst and only limited reaction occurs.

- 2) At 1750°C, an ignition occurs in which self-heating raises the sample temperature several hundred degrees (to >2000°C) and vapor phase burning occurs.

3) In subcooled water (30°C), violence due to agitation of the water causes fragmentation of the sample. The extent of reaction depends on the violence and time of quenching of individual particles.

4) In heated water, no fragmentations have been noted even though ignition and very extensive reactions do occur at the higher energies.

Experiments were also continued in TREAT to investigate the safety problems associated with the behavior of metal-clad, UO_2 -core fuel rods. Recent experiments have been conducted with single pins (0.5 in. long by 0.375-in. OD) of UO_2 -core fuel clad with Zircaloy-2. Three experiments were performed to extend to higher fission energy inputs the correlations previously obtained with single pins. The experiments were conducted at fission energy inputs of 375, 595, and 675 cal/g UO_2 and the pins reacted to the extents of 13%, 21%, and 68%, respectively. A comparison of the pressure-time records from all of the experiments performed with single UO_2 -core pins clad with Zircaloy-2 indicates that with a nuclear energy input less than 400 cal/g UO_2 the pressure rise rate is modest, being of the order of 100 psi/sec. For meltdowns with energy inputs of 500 cal/g UO_2 or more, the rise rate is invariably a few thousand psi/sec, increasing progressively with energy input. Between 400 and 500 cal/g, either behavior can occur. The final equilibrium pressure is the sum of the partial pressures of the hydrogen evolved, the water vapor, and helium at the temperature of the test capsule.

Experiments in TREAT using the scale-up autoclave were also continued. Three such experiments were performed: two with bundles of four Zircaloy-2-clad, vibrationally compacted UO_2 -core fuel rods (each rod, 9.5 in. long by 0.566-in. OD), and one with a bundle of three Zircaloy-2-clad, UO_2 -core (sintered pellets) fuel rods. The latter experiment was conducted with the rods suspended above a pool of water as a simulation of the conditions that would occur during a loss-of-coolant accident. The two experiments with vibrationally compacted UO_2 -core fuel rods were performed in the usual manner with the rods submerged in 30°C water, simulating a nuclear excursion.

In one of the experiments with vibrationally compacted UO_2 -core fuel, each rod was fabricated with 1500 psia helium internal gas pressure to simulate fission product gases. The helium in the rods of the other bundle was at a pressure of 15 psia. Both bundles were subjected to approximately the same fission energy input (~ 470 cal/g UO_2). The extents of metal-water reaction and the average particle sizes of the fragmented fuels were nearly identical for the two bundles. The cladding temperature records, however,

indicated major differences in the two runs. For the rods with an internal helium pressure of 1500 psia, only about 30% of the total nuclear energy had been released when failure was indicated by the temperature record; apparently the high-pressure gas ruptured the cladding at a low temperature. For the rods with 15 psia internal helium pressure, approximately 85% of the total energy had gone into the rods when failure was indicated, apparently as a result of melting of the Zircaloy cladding. The peak pressures generated in these experiments with vibrationally compacted UO_2 were ~ 2.5 times as great as in similar experiments performed with sintered UO_2 -core fuel rods. The maximum pressure rise rates were ~ 100 times greater than in previous experiments with sintered fuels.

The experiment with the bundle of three sintered UO_2 fuel rods suspended above a pool of water was conducted to simulate certain aspects of a loss-of-coolant accident. The meltdown was achieved during a "flat-top" transient in which the fission heating remained reasonably constant over a period of about 12 sec. (This was in contrast to the normal TREAT pulsed transient in which heating is accomplished in less than 1 sec.) The cladding reacted to the extent of 40%. Portions of the cladding were found in their original form, but the UO_2 core had apparently melted and flowed out of the cladding. The portions of the cladding that had melted did not separate from the unmelted portions. Since the energy developed in this experiment (560 cal/g UO_2) was sufficient to vaporize the UO_2 and the time scale (12 sec) was relatively short, the experiment was not an exact simulation of a loss-of-coolant accident. Therefore, the extent of reaction is not directly comparable to what might be expected in such a situation. Nevertheless, the appearance of the residue gives some indication of the meltdown model that must be considered in the analysis of this type of incident.

Fast Reactor Safety Studies. The program of studies of potential problems in the field of fast reactor safety has continued. As part of this program, studies have been made of the interaction of fuel and cladding materials with molten sodium. An initial survey study, in which small heated samples of fuel or cladding materials were dropped into heated sodium, showed that molten cladding metals fragmented upon contact with the sodium. The mechanism that was proposed for the fragmentation is now being examined further by determining the mean particle sizes of the various fragmented metal residues, particularly those of the type 304 stainless steel samples. The residues of the stainless steel samples dropped into sodium at 250°C exhibited fragmentation at drop temperatures of

1500°C or greater, with the mean particle size decreasing to about 10 mils for samples dropped at temperatures above 2000°C. Stainless steel samples dropped into higher temperature sodium exhibited an even greater decrease in particle size; for sodium temperatures of 720 and 820°C the average particle sizes were 6 and 3 mils, respectively. Fragmentation of stainless steel in molten lithium was slightly less extensive than in sodium under similar conditions, whereas fragmentation in potassium was substantially the same as in sodium.

Studies of transient boiling heat transfer are continuing. The research is directed toward obtaining the information necessary to predict the magnitude of explosive pressures generated when hot fuel materials are suddenly dispersed into liquid coolant. Both water and liquid sodium coolants are of interest, and studies of forced convection film boiling from spheres are being carried out in both media. In order to better understand the phenomena and to correlate the data of the experiments, an attempt has been made to describe film boiling from a moving sphere in mathematical terms. A differential equation has been derived that gives the variation of the vapor film thickness around the sphere and includes the effects of both thermal radiation and subcooling in the liquid. However, a closed form solution has not been found and numerical methods will be required for the solution of the equation. A special case of this equation was solved analytically.

Experiments have been performed with the swinging-arm apparatus in which a heated nickel ball is rapidly passed through a pool of water. The temperature drop of the ball as it passes through the water is recorded as a function of initial ball temperature, water temperature, ball velocity, path length, and immersion time. These data are fed to a computer along with appropriate physical properties, and calculations are made which result in values of heat flux, heat transfer coefficient, and an average temperature of the ball surface. Additional experiments have been completed with a 1/4-in. dia. nickel ball moving through water at 12 to 13 ft/sec. Initial temperatures of the ball ranged from 150 to 1000°C and a path length of 21.6 in. was employed. The runs were made in water at 23 and 60°C. In these experiments the ball, which was attached to the end of a stiff wire, was pushed through the water. (In previous work the sphere was pulled through the water by means of the thermocouple wires attached to opposite sides of the sphere.) Computed results yielded a consistent set of heat flux values and heat transfer coefficients which compared well with previous data. However, in experiments with spheres that were pushed, a peak in the

heat fluxes and one in the coefficients were noted that were not apparent in the previous work. This difference is probably the result of differences in the fluid flow around the pushed and pulled spheres, but it is not as yet understood quantitatively. Additional experiments with other ball materials and under other experimental conditions are required before an overall correlation of the results can be attempted.

A motorized version of the swinging arm apparatus has been constructed in an inert atmosphere box and is being used to study forced convection boiling from spheres in sodium. Initial experiments with 1/2-in. dia. tantalum spheres passing through 300°C sodium have been carried out. The data, which consist of temperature-time histories of a point near the surface of the sphere, have been reduced by computer to give surface heat flux information.

Studies have continued of the high temperature physical properties of materials that are important in the field of reactor safety. Experiments to measure the specific heat of molten UO_2 are progressing. The initial work has consisted of tests of the suitability of tungsten as an encapsulation material at temperatures above the melting point of UO_2 . Tests have been carried out using a wide variety of sources of tungsten and in no case was gross attack of the container observed. One crucible made from wrought tungsten tubing and filled with UO_2 was heated to about 3350°C for two minutes. A metallic precipitate (identified as tungsten by metallographic examination and electron microprobe analysis) was observed in the oxide, as has been the case in many of the tests. Chemical analysis showed the O:U ratio to be unchanged from the initial $\text{UO}_{2.00}$ and revealed the presence of only 1.1 w/o tungsten in the residue.

The experimental determination of the extent of fuel migration and segregation in mixed uranium-plutonium fuels is continuing. A significant degree of segregation could seriously inhibit the effectiveness of Doppler broadening as a shut-down mechanism in an operating reactor. Tests of a gradient furnace for the migration studies are in progress. A vacuum system suitable for use with the furnace in a plutonium glove-box has been built and tested. Tungsten foil heaters have proven to be more reliable than tantalum foil heaters in long-term operation of the furnace with UO_2 pellets; in these tests, the upper surface of the pellet was held at 2000°C while the bottom surface was about 600 to 800°C lower. Extended-use tests of the apparatus employing ceria-urania pellets are proceeding satisfactorily.

An experimental study of the transient pressure and the aerosol produced by the liquid sodium-air reaction in simulated spray-type accidents has also been ini-

tiated. As part of this study calculations have been carried out for equilibrium conditions in sodium-air and sodium-air-water mixtures using a computer program designed to minimize free energy. The previous hand calculations of Baker and Tevebaugh were repeated assuming the air to be initially at 25°C and 12.2 psia with the sodium at 427°C. Calculations were also performed with the air assumed to be initially at a pressure of 14.7 psia. These calculations were made for both dry air and for air saturated with water at 25°C. The calculations were also performed assuming that NaO was not formed. Maximum pressures and temperatures calculated were not very different from those given by Baker and Tevebaugh. The maximum temperature calculated was 1990°C for a mixture of 5 gram atoms Na/mole O₂, whereas the maximum pressure was 133 psia at 7 gram atoms Na/mole O₂ (dry air at 14.7 psia, NaO formed). The effect of NaO formation was found to be small; the largest change of temperature noted was an increase of 40°C by excluding NaO in dry air at a ratio of 5 gram atoms Na/mole O₂. Adding water had the effect of lowering both the maximum temperature and pressure attainable.

Experimental measurements of the sodium-air reaction will also be carried out. A pneumatically operated piston device suitable for spraying about 15 g of molten sodium into an air-filled enclosure has been constructed and is being tested with water. Experiments with sodium will begin upon completion of the construction of dry box facilities.

Metal Oxidation and Ignition Kinetics. A brief series of burning experiments were performed with plate specimens (thickness 0.12 to 0.20 in.) having the following nominal compositions:

U, 19.6 w/o Pu, 2.5 w/o Mo (SEFOR material)

U, 25 w/o Pu, 2.5 w/o Mo

U, 25 w/o Pu, 3 w/o Ti

These studies were designed to determine specifically whether self-sustaining or propagating combustion could be induced in freely suspended, unclad plates of these materials. Specimen plates (0.5 by 0.5 in.) were heated rapidly by induction to temperatures from 600 to 1100°C to determine whether a self-sustaining reaction could be initiated. Rectangular specimen plates (2 by 0.5 in.) were heated only at the lower end to determine if a propagating reaction could be initiated. The results of the study can be summarized as follows:

1. Molybdenum-containing alloy specimens that were heated rapidly to temperatures from 900 to 1200°C did not undergo a self-sustaining reaction. (Overall reaction during the heating-cooling cycle was less than 12%.) However, heating in the range from

600 to perhaps as high as 900°C resulted in a self-sustaining reaction which continued to sample exhaustion (50 to 60 min). During this time the temperature of the sample remained constant in the range 600 to 660°C. The sustained reaction could be terminated by rapidly increasing the temperature to 1000°C with a burst of induction power.

2. There was no apparent effect of plutonium concentration in the range 20 to 25 w/o or of carbon content from 160 to 1130 ppm for the molybdenum-containing ternary alloys.

3. Titanium-containing alloy specimens followed the same general pattern as the molybdenum-containing alloys, except that the titanium-containing alloy specimens reacted more extensively during experiments in which the reaction was not sustained. About 200 min was required for complete reaction after initiation of self-sustained reaction; the temperature was self-regulating at 360 to 370°C.

4. Propagating reactions were generally not induced in the rectangular specimen plates. Only in one experiment (with a molybdenum-containing alloy) was a self-sustaining reaction initiated in the unheated upper end of a rectangular specimen by heating of the lower end.

5. The self-sustained oxidation reactions can be explained in terms of a dual regime of linear oxidation kinetics where there is hysteresis in the transitions between regimes. The postulated kinetic phenomenon has been observed in studies with pure plutonium. It was concluded from the kinetic analysis of the reaction that the existence of self-sustained oxidation is very dependent upon factors influencing heat loss rates from the reacting specimens.

V. Energy Conversion (pages 214 to 225)

Investigations on regenerative electrochemical systems for the conversion of heat into electrical energy have been continued. The program is divided between physical-chemical laboratory studies and engineering considerations.

Regenerative Emf Cells—Physical-Chemical Laboratory Studies. In the intermetallic studies, the emf-temperature-composition characteristics of the sodium-bismuth bimetallic concentration cell have been determined using two additional cells (50 and 60 a/o Na) with solid NaCl electrolytes. The observed potentials versus a pure sodium anode for these and earlier reported cells ranged from 0.34 to 0.74 volt at temperatures between 520 and 1050°K and for cathode compositions between 10 and 60 a/o sodium in bismuth.

Studies have been initiated to measure the conductivities of lithium hydride-lithium halide binary systems. These systems, which are being considered as the electrolyte for a lithium hydride emf cell, exhibit positive deviations from ideality for the lithium hydride portion of the electrolyte. These positive deviations, generally indicative of association, have been interpreted as indicating the presence of dimeric lithium halide species. Conductance measurements may result in a better understanding of the nature of the species in these fused salt systems.

Total vapor pressure, vapor composition, and vapor density measurements have been made for the sodium-lead intermetallic system to delineate the liquid-vapor equilibria in this system. Information of this type is necessary for the design of the regenerator of a bimetallic concentration cell. The total pressure measurements have been made by a quasi-static technique, while the vapor compositions and densities have been determined by the transpiration technique.

The emf's that would be required in order to regenerate a sodium-lead cell electrochemically have been calculated from the liquid-vapor equilibrium data. For a 70 a/o lead cathode composition, the equivalent emf at a regeneration temperature of 850°C is 0.323 volt, whereas the emf cell would produce 0.335 volt (estimated open circuit voltage) at 425°C. Thus, the results are unfavorable for electrochemical regeneration, but do not preclude thermal regeneration.

The partial molar free energy of sodium was calculated from the temperature dependence of the sodium activity for several sodium-bismuth systems.

A better understanding of the structure of molten salts may be gained from the identification of species and molecular association in these salt systems. For this purpose, a laser-excited Raman spectrophotometer has been designed and constructed. The source of excitation light is a continuous He-Ne gas laser with a nominal power output of 50 mw at 6328 Å. In testing the apparatus prior to its use in the study of fused salts, the isotopic fine structure of the 459 cm^{-1} carbon tetrachloride line and the pure rotational spectrum of gaseous oxygen were obtained. The data compared favorably with the same spectra obtained with conventional Raman spectrophotometers.

Regenerative Emf Cells—Engineering Studies. An experimental sodium-bismuth bimetallic closed cell apparatus without a thermal regenerator was operated successfully as a battery for 17 months; at this time the experiment was terminated owing to accidental shorting of heater transformers. The cell was electrically recharged about every two days during the 17-month period.

An experimental sodium-lead bimetallic cell apparatus with an attached thermal regenerator has been operated for approximately 100 hr. The cell and regenerator are made of stainless steel, and the cell has a frozen electrolyte-silicone rubber pressure seal. A cell current of 2.5 amp at 0.28 volt has been achieved at a cell temperature of 550°C and a regenerator temperature of 780°C.

Corrosion studies are continuing to determine the effect of liquid cathode metals (bismuth, tin, and lead) on materials of construction for cell components. Both static and dynamic tests are being conducted. A molybdenum-30 w/o tungsten loop was fabricated and tested for bismuth compatibility with hot and cold leg temperatures of 1050°C and 700°C, respectively. The loop developed linear fractures after 2488 hr of operating time; the cause of these fractures is under investigation.

VI. Nuclear Constants (pages 226 to 228)

Neutron cross section measurements related to the fast reactor program are being continued. Radiative capture cross sections of ^{89}Y as a function of neutron energy are reported, and the results compared with theoretical calculations. Measurements have begun of the radiative capture cross sections of ^{85}Rb , ^{86}Sr , ^{87}Rb , and ^{41}K as a function of neutron energy. Various uranium and plutonium isotopes are undergoing irradiation in EBR-II for measurement of the capture-to-fission ratios of these isotopes. Three of a total of eight sample-containing subassemblies have received the required irradiation and have been removed from the reactor; the others will be in the reactor for about six more months.

VII. Analytical Research and Development (pages 229 to 232)

The program for the development of analytical methods for the determination of burnup of fast reactor fuels and for the measurement of fast fission yields is continuing. A method for determining burnup by total rare earth analysis is being developed. After separation from interferences by precipitation and ion exchange, the rare earths are determined by a compleximetric titration. The compatibility of the ion exchange separation and the titration has been demonstrated; 500 μg of rare earths have been determined with an accuracy of $\pm 0.6\%$.

Neutron activation analysis is being investigated as

a method for determining the fast fission yield of praseodymium-141. Using manganese-55 as the internal flux monitor, 120 to 200 μg of praseodymium have been determined with a precision of $\pm 0.7\%$. Procedures for separating praseodymium-141 from interferences are described.

Previously reported values for the uranium-235 fission yields of cesium-133, cesium-137, and technetium-99 have been revised as a result of refinements in the calculations. The revised values are: cesium-133, $6.65 \pm 0.07\%$; cesium-137, $6.22 \pm 0.04\%$; technetium-99, $6.03 \pm 0.08\%$.

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SEMIANNUAL REPORT

I

Compact Pyrochemical Processes¹

Compact pyrochemical processes are nonaqueous processes that are being developed for the recovery and purification of fuels discharged from power reactors. Because inorganic, radiation stable materials are employed in these recovery processes, they can accommodate short-cooled, high-burnup ceramic fuels (such as oxides or carbides) and metallic fuels with a consequent reduction in fuel inventories. Such processes are suitable for small processing plants serving one or several reactors. The present indications are that the same process, with little or no change in the sequence of operations, could handle both core fuel containing about 10 to 20 w/o plutonium and blanket material containing 5 w/o or less plutonium.

These processes possess other general advantages for fast reactor fuels. Among these advantages are the avoidance or simplification of chemical conversions, the use of small process volumes (and, hence, compact processing equipment), the direct production of solid radioactive wastes, the alleviation of criticality problems because of the absence of aqueous solutions, and in some of these processes, the retention of valuable alloying elements in the fuel.

Pyrochemical processing has as its objectives the following: (1) removal of the bulk of the fission products, (2) extraction of the bred plutonium from the blanket, (3) enrichment of the core with plutonium, and (4) repair of irradiation damage. These objectives are achieved through separations of cladding material, uranium, plutonium, and fission products from one another. Because of the buildup of radioactive isotopes of uranium and plutonium in recycled fuel, it is unlikely that direct refabrication of the fuel will be possible, even with complete removal of the fission products.

In pyrochemical processes, the processing media generally consist of liquid metal and molten salt systems. The metal solvent systems are usually binary alloys of magnesium with zinc, cadmium, or copper. The salt systems consist of halide salts of alkali and alkaline earth metals. One of the newer concepts in pyrochemical processing under development employs

a salt transport separations step. Salt transport separations are based on the selective transfer of solutes (fissile and fertile materials) from one liquid metal solution (donor) to another (acceptor) by cycling a molten salt phase which acts as a carrier between the two metal solutions. Processes utilizing salt transport separations show promise of excellent separations of fission products from uranium and plutonium and high recoveries of uranium and plutonium.

An economic evaluation was made² of pyrochemical processing of the core and blanket of hypothetical fast breeder reactors that might be expected to be in commercial operation in about 1980. In this evaluation, conceptual processing plant designs were made and costs estimated for processing of oxide, carbide and metal fuels from reactors of a nominal 1000 Mw(e) size. The cases investigated were for close-coupled processing plants serving one and three reactors and for a central processing plant serving ten reactors in a 1000-mile radius. The evaluation involved a cost comparison of pyrochemical with aqueous and volatility plants for processing, waste disposal, and out-of-reactor fuel inventory. Significant cost advantages were shown for pyrochemical processing relative to aqueous for all fuels in the close-coupled plants. For the processing of metal fuel, pyrochemical processing was significantly cheaper than other processes for all cases investigated in this study. The cost advantages of pyrochemical processing had their sources in the relatively few items and small size of process equipment, in the short cooling time required for the discharged fuel before processing and in the concentrated, solid form of the high-level-activity fission product wastes. The study also indicated certain general advantages of close-coupled plants over central plants. The salt transport process concept, although not sufficiently developed to be used in the detailed cost estimates of the study, was considered to promise significant reductions in the cost of pyrochemical processing of ceramic fuels.

² M. Levenson, V. G. Trice, Jr., and W. J. Mecham, Comparative Cost Study of the Processing of Oxide, Carbide, and Metal Fast Breeder Reactor Fuels by Aqueous, Volatility, and Pyrochemical Methods, ANL-7137.

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

A. LABORATORY-SCALE INVESTIGATIONS (I. JOHNSON, R. K. STEUNENBERG, P. FINEMAN)

Laboratory-scale investigations of pyrochemical processes are being conducted to provide basic chemical data of process importance and to originate and evaluate new process concepts. During the period covered by this report the major effort has been devoted to the further development of a relatively new process concept that is referred to as a salt transport separation (see ANL-7125, pp. 21-22). Salt transport separations are based upon the selective transfer of solutes between two liquid metal solutions in mutual contact with a molten salt. Chemical investigations in

support of salt transport separations include (1) measurements of the distribution coefficients of cerium, plutonium and uranium between liquid alloys and molten salts, (2) determinations of the solubilities of uranium and plutonium in liquid alloys, and (3) investigations of the physical behavior of solid MgO in molten chloride salts. Studies were also conducted on the $\text{MgCl}_2\text{-MgBr}_2$ system and on the preparation of isotopically pure ^{24}Mg metal from ^{24}MgO for a nuclear physics research program.

1. Conceptual Salt Transport Process for Uranium-Plutonium Fuels (J. B. KNIGHTON, W. J. WALSH)

A conceptual pyrochemical process that is currently under investigation employs a salt transport step for the separation of uranium and plutonium. The process flowsheet outlined in Figure I-1 is a revised version of the one presented in the preceding report (ANL-7125, Figure I-1, p. 22). This process is designed to accommodate discharged core or blanket elements from fast

breeder reactors employing oxide or carbide fuels. The oxide preparation step would be replaced by a carbide preparation step in the case of carbide fuels.

After a decladding step, the plutonium separation in Figure I-1 involves four basic steps: (1) oxide reduction and partition, (2) salt transport separation of plutonium, (3) retorting, and (4) oxide preparation.

FIG. I-1. Conceptual Pyrochemical Process for Uranium-Plutonium Core or Blanket Fuel from Fast Breeder Reactor. (The oxide flowsheet is also applicable to carbide or metallic fuels with minor modifications.)

The uranium stream in Figure I-1 follows the plutonium stream through the first step, and is then separated from plutonium in the second step. Uranium is separated from the noble metal fission products and then oxidized to UO_2 . This latter separation step is discussed in more detail below since it may be different for core and blanket elements.

The oxide mixture from the decladding step is added to a MgCl_2 -bearing molten chloride salt. The oxide, suspended in the molten salt, is reduced by contacting the salt phase with a liquid Cu-Mg alloy. Under these conditions the alkali, alkaline earth and rare earth fission product elements partition strongly in favor of the salt phase, and are, therefore, separated from the uranium, plutonium, and the refractory and noble metal fission product elements. The salt, which also contains the solid MgO formed as a product of the reduction, is discarded as a waste.

The resulting Cu-Mg alloy which contains the uranium, plutonium, and the refractory and noble fission products enters the salt transport separation step. In this step the plutonium (and possibly some uranium) is transferred from the Cu-Mg alloy to a Zn-Mg alloy. The bulk of the uranium remains in the Cu-Mg alloy with the refractory and noble metal fission products. The Zn-Mg alloy is vacuum distilled to recover metallic plutonium, which is then converted to the oxide. If it is desirable to form a mixed plutonium-uranium oxide, as would be the case for core fuel, additional uranium might be added to the Zn-Mg-Pu alloy prior to vacuum distillation.

The Cu-Mg alloy containing the uranium from the salt transport step then enters the uranium separation step. The uranium is only sparingly soluble in the Cu-Mg alloy and is present largely as solid metallic uranium. Most, but not all, of the noble and refractory metal fission product metals are in solution in the Cu-Mg alloy. Depending upon the particular process requirements, decontamination of the uranium can be accomplished by either of the two following procedures. (1) In the case of blanket uranium, for example, decantation of the liquid Cu-Mg alloy followed by one or more washes of the solid uranium with liquid magnesium may provide adequate decontamination, since the quantities of fission products present at this point are small. (2) Should greater decontamination of the uranium be required, as may be the case for core-uranium, the composition of the Cu-Mg donor alloy can then be changed (removal of part of the magnesium by distillation is sufficient) to increase the uranium solubility so that the uranium can be transferred by means of a salt transport step to a Zn-Mg acceptor alloy. (In the separation of uranium and plutonium from the donor alloy, zinc-magnesium acceptor alloys of different compositions would be used, a high magnesium-low zinc alloy for the uranium and a high zinc-low magnesium alloy for the plutonium.) The noble and refractory metals remain behind in the Cu-Mg alloy. The Zn-Mg alloy is vacuum distilled to recover metallic uranium, which is then converted to the oxide.

2. Distribution of Elements Between Liquid Alloys and Molten Salts

In the pyrochemical processes currently under investigation, the basic separations of uranium, plutonium, and fission products are effected through differences in the distribution behavior of these elements between liquid alloys of magnesium and molten salts containing MgCl_2 . Three types of liquid alloys are required in the salt transport process, a donor alloy and two acceptor alloys. One of the acceptor alloys acts as a plutonium acceptor and the other as a uranium acceptor. Studies which have been made in order to evaluate several candidate donor alloys (Cu-Mg, Cu-Cd-Mg and Cu-Zn-Mg) are reported below.

a. DISTRIBUTION OF CERIUM, PLUTONIUM, AND URANIUM BETWEEN MOLTEN MgCl_2 AND CU-MG ALLOYS (J. B. KNIGHTON, K. R. TOBIAS)

To aid in the evaluation of liquid Cu-Mg solutions as donor alloys for the salt transport process, the dis-

tribution coefficients of cerium, plutonium, and uranium between molten MgCl_2 and liquid Cu-Mg alloys at 800°C have been measured as a function of the magnesium concentration of the alloys. The results of these measurements are given in Figure I-2. The cerium partitions strongly in favor of the molten salt, and the plutonium partitions somewhat in favor of the salt at low magnesium concentrations. The uranium tends to favor the liquid alloy. The break in each curve represents a composition range of the Cu-Mg alloy that is solid at 800°C because of the formation of an intermetallic compound, MgCu_2 (m.p. 819°C).

The separation of rare earth fission products from uranium and plutonium occurs during the oxide reduction step (Figure I-1). Therefore the reduction alloy, which serves later as a salt transport donor alloy, must also provide suitable distribution coefficient relationships for a rare earth-actinide separation. At an alloy composition of 6.5 w/o magnesium the cerium-plu-

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FIG. I-2. Distribution Coefficients of Cerium, Plutonium, and Uranium Between MgCl_2 and Cu-Mg Alloys at 800°C .

tonium separation factor³ is about 310 while the cerium-uranium separation factor is about 2240, thus affording the possibility of an excellent separation of the rare earth metals from the actinide metals. After the reduction step, the salt phase, which contains the rare earths and solid MgO , is discarded.

For rapid transfer of uranium from the donor alloy to the uranium acceptor alloy, the concentration of uranium in the molten salt in contact with the donor alloy must be significantly larger than the concentration in the salt that is in contact with the uranium acceptor alloy. These uranium concentrations in the salt may be computed from the product of the concentration of uranium in the alloy and its distribution coefficient. Since the donor alloy initially contains an excess of metallic uranium (gross composition about 16 w/o), the concentration of uranium in the liquid alloy will be set by its solubility. The solubility of uranium in a liquid Cu-6.5 w/o Mg alloy is about 3.5 w/o (ANL-7055, p. 38). Hence, the concentration of uranium in

the molten salt would be $3.5 \times 0.29 = 1.0$ w/o, where 0.29 is the distribution coefficient for uranium taken from Figure I-2. The corresponding concentration of uranium in the molten salt over the uranium acceptor alloy is about 0.01 w/o. Therefore, a reasonably rapid transfer rate would be expected.

A similar computation can be made for the transfer of plutonium, except that in this case all of the plutonium is in solution in the donor alloy. Since the initial plutonium concentration in the donor alloy is about 1.6 w/o and the distribution coefficient for plutonium is 2.1 (Figure I-2), the concentration of plutonium in the molten salt in contact with the donor alloy would be $1.6 \times 2.1 = 3.4$ w/o. The plutonium concentration in the molten salt over the plutonium acceptor alloy is about 0.1 w/o. Again a satisfactory transfer rate would be expected.

Adequate transfer rates and suitable rare earth-actinide separation factors can be achieved with a Cu-Mg alloy containing about 6.5 w/o magnesium. As plutonium or uranium is added to the donor alloy during the reduction or removed from it during the salt transport steps, magnesium is transferred in the opposite direction. Therefore, some means of maintaining the magnesium concentration in the donor alloy at about 6.5 w/o must be available. One possible method of maintaining the magnesium concentration at this level involves the use of a Cu-Mg alloy with an overall composition in the two-phase region between the Cu-Mg solid solution (~ 2 w/o Mg) and the liquidus (~ 6.5 w/o Mg). When magnesium is added to the system more copper dissolves, thereby maintaining the liquid phase at the liquidus composition. When magnesium is removed from the alloy, the precipitation of copper results in a constant liquid composition. At 800°C the overall gross composition of the copper-magnesium alloy can vary from about 2 w/o Mg to 6.5 w/o Mg and still maintain a liquid phase of 6.5 w/o Mg.

In summary, a Cu-6.5 w/o Mg alloy appears to offer excellent potential as a donor alloy for the salt transport process. This alloy affords the possibility of a good separation of the rare earth fission product elements from uranium and plutonium, and the indications are that the transport rates of uranium and plutonium from this alloy will be rapid.

b. DISTRIBUTION OF CERIUM, PLUTONIUM, AND URANIUM BETWEEN CaCl_2 - NaCl - MgCl_2 AND COPPER-6.5 w/o MAGNESIUM ALLOY AT 800°C (J. B. KNIGHTON, K. R. TOBIAS)

In order to achieve an adequate separation of rare earths from plutonium together with adequate plutonium recoveries during the oxide reduction step of

³ Separation Factor = $\frac{(\text{w/o Ce in Salt})/(\text{w/o Ce in Metal})}{(\text{w/o Pu in Salt})/(\text{w/o Pu in Metal})}$

The salt transport process, careful attention must be given to the distribution of rare earths and plutonium between the reduction salt and the Cu-Mg alloy. The rate of reduction is increased by a high concentration of MgCl_2 in the molten salt. On the other hand, the distribution coefficients of uranium, plutonium, and other fuel constituents between the molten salt and liquid metal phases also increase with increasing MgCl_2 concentration in the salt. Since the salt becomes a waste stream of the process, the concentrations of the fissile elements in the salt phase must be small in order to maintain their loss at acceptably low levels. Therefore, this process step must be optimized with respect to fissile element loss by slow and possibly incomplete oxide reduction (caused by low MgCl_2 concentrations) and loss by high concentrations in the waste salt (caused by high MgCl_2 concentrations).

The distribution of cerium, plutonium, and uranium between a salt (consisting of equimolar NaCl-CaCl_2

and varying amounts of MgCl_2) and Cu-6.5 w/o Mg alloy at 800°C was investigated. Results of these experiments are presented in Figure I-3. These data show regular increases in each of the distribution coefficient curves as the MgCl_2 concentration in the salt is increased. The rare earth-plutonium separation factor (309) remains essentially constant as the MgCl_2 concentration in the salt increases from about 10 to 100 m/o MgCl_2 .

These distribution data provide a basis for the selection of an optimum concentration of MgCl_2 in the salt for the reduction of uranium and plutonium oxides by Cu-6.5 w/o Mg alloy and for the rare earth-plutonium separation.

c. CO-DISTRIBUTION OF CERIUM, PLUTONIUM, AND URANIUM BETWEEN 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl AND Cu-Cd-Mg ALLOYS (W. KNOCH⁴)

Copper-magnesium alloys have been used in salt transport studies as donor alloys. Large separation factors between uranium, plutonium and rare earth

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FIG. I-3. Distribution Coefficients of Cerium, Plutonium, and Uranium Between CaCl_2 - NaCl - MgCl_2 Salt and Copper-6.5 w/o Magnesium at 800°C .

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FIG. I-4. Co-distribution Coefficients of Cerium, Plutonium, and Uranium Between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and (Cu-50 w/o Cd)-Mg Alloys at 600°C and 700°C .

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FIG. I-5. Solubilities of Cerium, Plutonium, and Uranium in (Cu-50 w/o Cd)-Mg Alloys and Corresponding Equilibrium Concentrations in 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl at 700°C.

fission products make this system attractive. Another advantage is the possibility of maintaining a constant magnesium concentration during the process. However, this system has the disadvantage that a relatively high operating temperature ($\sim 800^\circ\text{C}$) is required. The addition of cadmium to the binary Cu-Mg alloy and use of a lower-melting salt mixture would permit a lower operating temperature.

The distribution coefficients of cerium, plutonium, and uranium between 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl and (Cu-50 w/o Cd)-Mg alloys at 600 and 700°C were determined as a function of magnesium concentration in the metal phase. The results are given in Figure I-4. The uranium distribution coefficient for a 46 w/o Cu-46 w/o Cd-8 w/o Mg alloy at 700°C is about equal to that for a Cu-8 w/o Mg alloy at 800°C, although the uranium solubility in the metal phase and its equilibrium concentration in the salt in the latter system are higher by a factor of about four. A calculation made from the available data (Figure I-5), indicates that the operating temperature of the partition step in the salt transport process could be dropped to 650–700°C by using a Cu-Cd-Mg alloy instead of a Cu-Mg alloy. An increase in the magnesium concentration in the metal phase from near zero to about

8 w/o can be tolerated. The uranium concentration in metal and salt phases, which determine rate of uranium transport in the process, could be increased by using a salt of higher MgCl_2 content. The equilibrium uranium concentration in the salt above the saturated metal solutions is increased by a factor of three by changing the MgCl_2 concentration from 50 to 100 m/o.

d. DISTRIBUTION OF URANIUM BETWEEN 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl AND Cd-Zn-Mg ALLOY (J. B. KNIGHTON, K. R. TOBIAS)

The Cd-Zn-Mg system is being considered as a potential donor alloy for uranium transfer. The use of Cd-Mg alloys in salt-metal extraction procedures was proposed (ANL-7055, p. 40) and distribution coefficients of uranium and plutonium between 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl and Cd-Mg alloys were reported (ANL-7125, p. 25). The use of Cd-Mg solutions as a donor alloy in the salt transport process, however, has the disadvantage of low solubility of uranium, which results in low transfer rates. The addition of 10 w/o zinc to the Cd-Mg solutions improves the uranium solubility by a factor of about 2.5.

An experiment was conducted to determine the distribution coefficient of uranium between a 50 m/o MgCl_2 -30 m/o NaCl-20 KCl salt and Cd-Zn-Mg alloys. The specific region of interest was at low magnesium concentration, and a cadmium to zinc ratio of 9 to 1 was used to provide maximum uranium solubility in the alloy. The effect of temperature on the distribution coefficient was determined over the range of 448 to 650°C.

The data (Table I-1) show that uranium distributes to the salt (with a magnesium concentration of ~ 0.3 w/o in the alloy) in substantial concentrations (1.4 w/o U at 448°C to 9.5 w/o at 650°C). These results suggest some highly attractive features for process application, i.e., (1) low temperature of operation, (2) potentially high rates of uranium transfer, (3) a

TABLE I-1. DISTRIBUTION OF URANIUM BETWEEN 50 m/o MgCl_2 -30 m/o NaCl-20 m/o KCl SALT AND Cd-Zn-Mg ALLOY

Sample	Temp. (°C)	Metal		Salt (w/o U)	K_d , Distribution Coefficient
		w/o Mg	w/o U		
1	600	0.28	2.64	3.41	1.29
2	598	0.23	2.80	4.72	1.69
3	650	0.36	5.91	9.50	1.60
4	530	0.25	4.61	5.4	1.17
5	448	0.16	1.76	1.39	0.791
6	500	0.23	4.03	5.1	1.26

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FIG. I-6. Co-distribution Coefficients of Cerium, Plutonium, and Uranium Between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and (Cd-10 w/o Zn)-Mg Alloys at 600°C.

donor alloy consisting only of volatile components, and (4) the possibility of using series 400 stainless steels for containment vessels, transfer lines, pumps, etc.

The Cd-Zn-Mg system has the disadvantage that the equilibrium uranium concentration in the salt is very sensitive to small changes of magnesium concentration in the donor alloy. This system requires a method of maintaining a constant magnesium concentration. An external method for magnesium control could be devised. For example, magnesium could be removed from the donor alloy by chemical oxidation or by vacuum retorting. The rate of magnesium removal would have to equal the rate of magnesium transfer via the salt transport mechanism. It would then be possible to transfer uranium at temperatures as low as 450°C, presumably at very high rates.

e. CO-DISTRIBUTION OF CERIUM, PLUTONIUM, AND URANIUM BETWEEN 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl AND Cd-Zn-Mg ALLOY AT 600°C (W. KNOCH⁴)

The distribution coefficients of cerium, plutonium, and uranium between 50 m/o MgCl_2 -30 m/o NaCl -20

m/o KCl and (Cd-10 w/o Zn)-Mg alloys at 600°C were determined with varying magnesium concentrations in the alloy. The results are presented in Figure I-6.

Although the distribution coefficients of cerium, plutonium, and uranium are approximately the same in the systems Cd-Mg/50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and (90 w/o Cd-10 w/o Zn)-Mg/50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl , the actual solute concentrations in the metal and salt phases are much higher in the latter system (Figure I-7). The two curves given for the uranium solubility in the metal phase below about one percent magnesium result from the approach to equilibrium from two different directions in the multicomponent system. The lower solubilities were obtained when uranium metal was dissolved in the liquid alloy at 600°C, whereas the higher solubilities were obtained when a completely liquid alloy was allowed to cool from a higher temperature to 600°C. The concentration of uranium in the salt varies with the uranium solubility in the metal phase so as to yield a single curve of distribution coefficient versus magnesium concentration (Figure I-6). Thus, a (Cd-10 w/o Zn)-low Mg/salt system may become attractive as a donor alloy in a salt transport process

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FIG. I-7. Solubilities of Cerium, Plutonium, and Uranium in (Cd-10 w/o Zn)-Mg Alloys and Corresponding Equilibrium Concentrations in 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl at 600°C.

⁴ On assignment from the Institute für Kern- und Radiochemie, Technische Hochschule Braunschweig, Germany.

where low operating temperatures are desired. All constituents are sufficiently volatile to be removed by vacuum distillation. Furthermore, a Zn-Cd-Mg alloy with a low magnesium and a low cadmium content would represent a more favorable acceptor alloy for

plutonium in the salt transport process than does the presently proposed Zn-low Mg alloy. The ternary system would be a more selective acceptor alloy for plutonium and would, therefore, permit a better separation of plutonium from uranium.

3. Solubilities in Liquid Alloys

The solubilities of uranium, plutonium, fission product elements and structural metals in liquid alloys are of importance in the choice of suitable donor and acceptor alloys for the salt transport process, in determining the volumes of process streams, and in evaluating corrosion data. Data are presented below on the solubilities of uranium and plutonium in potential donor alloys.

a. SOLUBILITY OF URANIUM IN LIQUID Cu-Cd ALLOYS (J. B. KNIGHTON, G. E. KOVAL)

Since Cu-Cd-Mg alloys have potential use as a donor metal solvent in the salt transport process, a

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FIG. I-8. Solubility of Uranium in Cd-Cu Alloys.

few data were obtained on the solubility of uranium in Cu-67 w/o Cd and Cu-85 w/o Cd alloys (nominal compositions). These data are presented in Figure I-8. Also included for comparison is the solubility of uranium in pure cadmium.⁵

The data indicate a general decrease in the uranium solubility as the copper concentration is increased. However, these uranium solubilities are believed to be sufficiently high for process purposes.

b. SOLUBILITY OF PLUTONIUM IN LIQUID Cu-Mg ALLOYS (W. KNOCH⁴)

The solubility of plutonium in liquid Cu-Mg alloys was determined at temperatures between 500 and 800°C (Figure I-9). No attempt was made to identify the solid phases or locate phase boundaries other than the liquidus lines represented by the solubility curves in the ternary diagram. However, the curves reflect the shape of the solid phase region and the compounds formed in the Cu-Pu system.⁶ The miscibility gap of the Mg-Pu binary system⁷ extends well into the ternary Cu-Mg-Pu system. The limiting line of liquid immiscibility is essentially independent of temperature between 500 and 700°C. Above 700°C, the data indicate a retrograde solubility of plutonium in the magnesium-rich phase. The highest solubility of plutonium between 500 and 800°C was in the range of 55 to 60 w/o at Cu:Mg ratios of about 1 (weight percent basis). The copper-rich liquid solutions at temperatures around 800°C are of particular interest in pyrochemical reprocessing applications. Between 8 and 10 w/o Mg the plutonium solubility increases rapidly up to about 60 w/o.

⁵ A. E. Martin, I. Johnson, and H. M. Feder, Trans. Met. Soc. AIME **221**, 789-791 (1961).

⁶ R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill Book Company, New York (1965), p. 379.

⁷ Ibid, p. 596.

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FIG. I-9. Solubility of Plutonium in Cu-Mg Alloys.

4. Magnesium Chloride-Magnesium Bromide System (J. FISCHER, J. J. HEIBERGER, R. D. WOLSON)

The liquidus temperature was determined at two compositions in the system $\text{MgCl}_2\text{-MgBr}_2$ to ascertain if there is a low-temperature liquid region. Such a region would be of process interest in that the high magnesium ion concentration in the salt phase, which gives high distribution coefficients, could be maintained at lower process temperatures.

A $\text{MgCl}_2\text{-MgBr}_2$ mixture containing 60.1 m/o MgCl_2 had a liquidus temperature of 703°C and solidified completely at 691°C. A mixture containing 40.1 m/o MgCl_2 solidified completely at 690°C. This latter point is probably close to the minimum of a solid solution loop. This system appears to be similar to the KBr-

KCl system,⁸ which forms a continuous series of solid solutions with a minimum at 734°C and 40 m/o KCl .

An X-ray diffraction pattern of the solidified 40.1 m/o MgCl_2 mixture was different from that of pure MgCl_2 . The existence of a solid solution was not verified by X-ray diffraction because no pattern for MgBr_2 was available.

Since no liquidus region below 700°C was found in this region of the $\text{MgCl}_2\text{-MgBr}_2$ system, it appears to offer no significant advantage over MgCl_2 alone (m.p. 716°C) as a process salt.

⁸ A. G. Bergman and M. B. Tokareva, *Zhur. Neorg. Khim.* **2**, 278 (1957).

5. Magnesium Oxide Removal from Reduction Salt (D. A. WENZ, R. D. WOLSON)

The first step after decladding in current pyrochemical methods for the reprocessing of oxide fuels is the reduction of the oxide from a molten salt slurry by a Cu-Mg alloy. This reaction produces insoluble MgO as a by-product in the molten salt. In order to reuse this salt, removal of most of the MgO is necessary.

A sample of salt resulting from the reduction of UO_2 by Cu-Mg alloy was examined to characterize the MgO particles. The salt sample was dissolved in water and the insoluble portion was dried and studied microscopically. The MgO was identified by its insolubility in water, its refractive index, its color, and the isotropic nature of its crystals. The oxide particles were of a relatively uniform size; the majority were below 5μ in diameter and the largest, about 10μ .

One possible method of separating solid MgO from the salt is to allow the oxide particles to settle to the bottom of the salt, and then to decant the supernatant salt. In order to determine the settling behavior of the MgO, a sample of the reduction salt containing MgO was placed in a quartz tube, heated to 500°C under a helium atmosphere, stirred, and then allowed

to stand. Visual observation of the melt showed that a minimum of about two hours was required for the insoluble material to settle, leaving an essentially clear supernatant salt which consisted of about three-fourths of the total salt volume. The boundary between the bed of solid MgO and the supernatant liquid salt was sharply defined. Microscopic examination of a reduction salt that had been allowed to stand at 500°C for about six hours indicated that no increase in the MgO particle size occurred during this time.

Analyses of the two layers of the settled salt showed that the supernatant salt contained only 0.25 w/o MgO, whereas the lower layer contained 22 w/o MgO. The MgCl_2 content of the supernatant salt after MgO had settled was the same as in the original salt before the reduction. The latter result eliminates the possibility that significant amounts of MgCl_2 might be removed from the salt by formation of insoluble magnesium oxychlorides. Thus, it appears that decantation of the supernatant salt after settling of the insoluble oxide is a possible method for recovering salt for recycle.

6. Preparation of ^{24}Mg Metal from ^{24}MgO (N. R. CHELLEW, J. D. SCHILB)

Isotopically pure (99.91%) ^{24}Mg metal, suitable for use in neutron-scattering and polarization experiments, was prepared by the thermal reduction of ^{24}MgO . The preparative method involved the simultaneous high-temperature (1150°C) reaction of ^{24}MgO with aluminum and CaO, and the vaporization of the product metal in vacuum according to the reaction:

By the use of an excess of aluminum, i.e., 99–150%

over that required by the above equation, yields of 98.3% (std. dev. $\pm 1.2\%$) were obtained. Mass spectroscopic analyses of the product showed no dilution of the ^{24}Mg isotope by ^{25}Mg or ^{26}Mg . (Natural magnesium contains 79 w/o ^{24}Mg , 10 w/o ^{25}Mg , and 11 w/o ^{26}Mg .) The principal metallic impurities in the product were 0.9 w/o calcium, 0.2 w/o sodium, and 0.01 w/o or less aluminum. All other elements detected were present in amounts approximating the limits of detection by emission spectrographic analysis.

B. ENGINEERING-SCALE INVESTIGATIONS (R. D. PIERCE, R. K. STEUNENBERG, P. FINEMAN)

Engineering studies are being conducted to develop the technology required for plant-scale application of pyrochemical processes. The major portion of this effort is devoted to investigations of process concepts on a pilot-plant scale, the present emphasis being on salt transport separations. These separations are based on the selective transfer of solutes between two liquid metal solutions in contact with a molten salt. Explora-

tory experiments on oxide reduction and salt transport separations are being performed, pilot-scale equipment is being developed, and materials of construction are being evaluated. These investigations are expected to lead to the design and operation of a pilot plant for the recovery of uranium and plutonium from simulated fast breeder reactor oxide fuel.

1. Engineering Studies of Salt Transport Separations (W. J. WALSH, I. O. WINSCH, T. F. CANNON, J. D. ARNTZEN, P. MACK, K. NISHIO, F. G. TEATS)

Engineering work related to the development of salt transport separations is under way. In the initial tests, attention was focused on the transfer of uranium,

of ~6 kg of uranium oxide and ~0.5 kg of oxides of cerium, zirconium, molybdenum, palladium, and ruthenium. These tests were conducted in pilot-plant equipment originally used in the studies of the EBR-II skull reclamation process (ANL-7125, pp. 32-35). The objectives of these experiments were to demonstrate the feasibility of salt transport separations, to identify the major engineering problems involved, to determine the fission product decontaminations obtainable, and to provide a clearer understanding of the salt transport step.

A schematic diagram of the equipment is given in Figure I-10. In order to simulate process conditions, the uranium and fission product elements were charged to the process as oxides and a reduction step was performed. The oxides were suspended in a MgCl_2 -based salt phase⁹ and reduced at 830°C by Cu-10 w/o Mg alloy, thereby precipitating the bulk of the uranium

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FIG. I-10. Schematic of Salt Transport Equipment.

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FIG. I-11. Theoretical Rate of Uranium Transfer in the System: Cu-Mg/ MgCl_2 /Zn-Mg.

which is the rate-limiting step for most versions of the salt transport process. In two experiments (Runs USTP-2 and -3), the reduction and salt transport steps were carried out at 830°C to recover uranium from an unirradiated charge consisting of a mixture

from the liquid metal solution in elemental form. After a four-hour reduction period, the salt (contain-

⁹ Salt composition: 30 m/o MgCl_2 -30 m/o NaCl-40 m/o KCl in USTP-2; 47.5 m/o MgCl_2 -47.5 m/o CaCl_2 -5 m/o CaF_2 in USTP-3.

FIG. I-12. Calculated Rates of Uranium Transfer for Continuous Salt Transport Systems.

ing principally cerium, MgO, and unreduced uranium) was removed and the concentration of unreduced uranium was determined. The amount of reduced uranium available for the following partition step was calculated from a material balance. Optimization of the reduction step was not undertaken in the experiments.

After completion of the reduction step and removal of the salt, the system consisted of 10 kg of a liquid metal phase composed of Cu-5.5 w/o Mg-5.5 w/o U, 12 kg of precipitated copper, and 4 kg of precipitated uranium. In the salt transport step, uranium in the molten Cu-Mg donor alloy was transferred incrementally to a molten Mg-35 w/o Zn acceptor alloy by cycling molten MgCl_2 between the two liquid alloys, which were in adjacent vessels. The temperatures of the donor and acceptor alloys were maintained at $\sim 850^\circ\text{C}$ and $\sim 780^\circ\text{C}$, respectively. The charge of molten MgCl_2 was pressure-transferred alternately from one alloy to the other through a heated transfer line. In each vessel, the salt and metal phases were mixed to promote chemical equilibration; the phases were

then allowed to separate by settling. The equilibration and settling times were 6 and 10 min, respectively, in the vessel containing Cu-Mg alloy and 6 and 5 min in the vessel containing Zn-Mg alloy.

A calculation was made, for this particular system, of the theoretical quantity of uranium transported as a function of the number of cycles completed. The results are presented in Figure I-11. The transfer proceeds at a constant rate until the last of the precipitated uranium goes into solution. The transfer rate then decreases steadily and the uranium recovery asymptotically approaches a value of 99.7%. The rate of uranium transfer during the constant rate period is approximately proportional to the quantity of salt transferred per cycle, the uranium solubility in the Cu-Mg alloy, and the distribution coefficient of uranium in the Cu-Mg/ MgCl_2 system. During the diminishing rate period, the fraction of uranium transferred per cycle is a function of the uranium distribution coefficients in the Cu-Mg/ MgCl_2 and Zn-Mg/ MgCl_2 systems, the relative weights of the salt and metal phases, and the phase transfer efficiency. The value of the asymptote is determined by the amount of uranium remaining in the MgCl_2 after equilibration with the Mg-Zn alloy.

The results of the first salt transport experiment (USTP-2) showed the uranium transfer to proceed in general accord with the curve shown in Figure I-11. Analyses of the salt phase indicated that the uranium transfer rate was constant at $\sim 1/3$ kg/cycle for the first 12 cycles. During the 12th cycle, the last of the precipitated uranium went into solution and the diminishing transfer rate that had been predicted was observed in cycles 13 and 14. The run was terminated after the 14th cycle. Analytical results showed that 4.1 kg (or 88% of the reduced uranium) had been transferred during the 14 cycles. In run USTP-3 entrainment of the Zn-Mg acceptor alloy in the molten salt resulted in a 50% increase in magnesium concentration in the Cu-Mg-U alloy. This high magnesium concentration caused the uranium distribution coefficient and solubility in the donor alloy to decrease, with the result that the uranium transfer rate was much lower. This high entrainment was the result of an operating procedure and is not expected to be a problem in subsequent runs.

Fission product removals were very satisfactory in these tests. By washing the precipitated uranium product with a Mg-20 w/o Zn alloy, overall removals of greater than 99.9% were achieved for zirconium and the noble metal fission product elements without incurring appreciable uranium losses. A product wash step after completion of run USTP-2 resulted in the

removal of greater than 90% of the impurities that were transferred with the uranium. The effectiveness of the wash step appeared to be limited only by the phase transfer efficiency. No detectable uranium entrainment occurred in this step.

The principal engineering problem encountered in these tests was contamination of the uranium product by copper *via* an entrainment mechanism. A study is under way to determine effective methods of decreasing the amount of copper entrained during the salt transport step. However, the copper contamination can also be reduced to an acceptable level by the simple product-washing procedure described above.

It is believed that these experiments have successfully demonstrated the feasibility of the salt transport principle on an engineering scale. Additional experi-

ments of this type will be made to determine the uranium recovery and purity which are attainable and to obtain additional kinetic data for the reduction and salt transport steps. In addition, work has begun on the development of continuous and semi-continuous equipment which offers the promise of higher transfer rates for the salt transport process. These developments will lead to the design and fabrication of pilot-plant equipment. As an example, Figure I-12 gives the theoretical uranium transfer rate as a function of solution volume and salt circulation rate (based on the available kinetic data) for the case of continuous salt circulation between two liquid metal alloys that are being mixed. As expected, these uranium transfer rates are higher than those calculated for equivalent batch-contact systems.

2. Salt Pump Loop (T. R. JOHNSON, F. G. TEATS, L. F. DORSEY, A. C. RASHINSKAS)

An instrumented loop of type 304 stainless steel in which molten chloride salt is circulated has been constructed and operated. The purposes of operating this equipment are to investigate the feasibility of pumping liquid salts with a centrifugal pump, to test the equipment and various instruments, and to determine whether pumped salt loops are suitable for pilot-plant and plant-scale use. A diagram of the loop is shown in Figure I-13. The principal components of the loop include a centrifugal pump, a freeze valve, a drain-fill tank, an inductance pressure tap, a bellows-sealed throttling valve, and an orifice flow meter. The pump was obtained from Oak Ridge National Laboratory where pumps of this type (LFB) were used to circulate molten fluoride salts in small test loops in connection with the Molten Salt Reactor program. The pump has been described in an ORNL report.¹⁰ The pump is a sump type with an overhung vertical shaft, the upper portion of the shaft being cooled and lubricated by circulating oil. The pumped salt is isolated from the oil and from impure atmospheres by a face seal of graphite rotating on hardened steel. A salt-lubricated, hydrostatic bearing supports the shaft above the impeller. The salt discharge is directed downward and is centered with respect to the pump shaft. The impeller is $3\frac{7}{16}$ in. in dia. and the depth of molten salt above the impeller in the 6-in. dia. sump tank is about 3 in. When rotating at 3000 rpm the pump is capable of delivering 3 gpm against a fluid head of 24 ft.

The loop is filled from and drained into an 8-liter tank through a freeze valve. The tank is filled to a depth of 1 in. with a Cd-30 w/o Mg alloy and to a total depth of 11 in. with a salt (50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl) which has been purified by contacting it with Cd-Mg alloy at 550–600°C, followed by filtration at 500°C to remove MgO and any other insoluble impurities. A drawing of the freeze valve is shown in Figure I-14. This device consists of a section of $\frac{1}{2}$ -in. OD stainless steel tubing that was flattened to form a rectangular passage having a minimum dimension of $\frac{1}{16}$ in. The rectangular cross section allows the tube to expand when salt is remelted within the valve. The valve is closed by passing gas around the tube to freeze the contained salt. The gas follows a circuitous path around and through copper fins brazed to the steel tube. The valve is opened by stopping the gas flow and energizing a resistance heater wrapped around the copper fins. A second, longer heater placed around the inner heater maintains the temperature of the cylindrical ends of the valve above the freezing point of the salt.

An experimental induction pressure device is used to measure the fluid pressure on the upstream side of the throttling valve. The salt pressure is determined by measuring the gas pressure required to maintain a static salt level at a specific location in a vertical leg of the loop. A hollow stainless steel ball within the vertical tube floats on the surface of the salt, and the ends of the tube are tapered to contain the ball. The position of the ball, and hence of the salt-gas interface, is detected by mutual inductance coils wrapped around the vertical tube. The operating principle of

¹⁰ J. L. Crowley, W. B. McDonald, and D. L. Clark, Design and Operation of Forced-Circulation Corrosion Testing Loops with Molten Salt, ORNL-TM-528, May 1963.

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FIG. I-13. Molten Salt Pump Loop.

this coil is similar to that used in the induction liquid level probe previously developed¹¹ for molten metal-molten salt systems. Because of the relatively low electrical conductivity of the salt, the mutual inductance of the coils is not affected significantly by the presence of the salt within the windings. The ball and the vertical tube constitute a double-ended check valve that, in the event of improper gas pressure regulation, prevents gas from entering the loop and salt from rising into the gas pressure lines. Because the checking action is not absolutely effective, a modified freeze valve was placed above the inductance pressure tap to insure that no salt reaches the gas manifold.

The throttling valve is a commercially available, all-welded, bellows-sealed, needle valve. The orifice

¹¹T. R. Johnson, F. G. Teats, and R. D. Pierce, An Induction Probe for Measuring Liquid Levels in Liquid Metals, ANL-7153, 1966.

flowmeter is also a commercial item. The pressure drop across the orifice is measured by means of diaphragms connected by NaK-filled lines to a differential pressure transmitter. The flow meter was calibrated with water. To prevent breakage of the diaphragms by melting salt, they are located above the line to allow complete drainage of salt when the loop is shut down.

The two vertical lines and the bottom horizontal line of the loop are $\frac{1}{2}$ in. OD tubing. The top horizontal line is $\frac{1}{2}$ -in. schedule 40 pipe. The loop and all instruments are made of 304 stainless steel except the pump, which is made of INOR-8. The latter alloy, which was developed by Oak Ridge to contain molten fluoride salts, has the nominal composition of 17 w/o Mo, 7 w/o Cr, 5 w/o Fe, several minor constituents, and the balance Ni. Most of the connections in the loop are welded, but three compression fittings are used, as shown in Figure I-13.

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FIG. I-14. Freeze Valve for Molten Salt Loop.

To date, the salt-pump loop has been started up and shut down three times for a cumulative operating time of 160 hr. The duration of each of the three runs was 45 to 65 hr. The average temperature of the salt was 510 to 520°C, except for the last 30 hr when it was increased to 540 to 550°C. The average pumping rate in all of the runs was 0.8 gpm, but flow rates up to 3.5 gpm were attained at impeller speeds well below the design limit.

The pump characteristics (fluid head developed versus fluid flow rate at various impeller speeds) were measured at 540°C. The outlet pressure of the pump was measured with the inductance pressure tap, and the salt flow rate with the orifice flowmeter. The characteristics were typical of centrifugal pumps; at a given impeller speed the pressures developed in the chloride salt were about 15% lower than those reported for similar pumps with fluoride salts.¹⁰

Other components of the loop operated routinely. The freeze valve which held the salt in the loop underwent about 15 open-close cycles without any apparent change in performance. The valve could be opened in less than three minutes and closed in less than one minute.

Chemical analyses of the salt in the loop, after 110 hr of loop operation, showed only slight changes in the concentration of several possible contaminants. Sampling was accomplished after draining the salt from the loop through the freeze valve into the drain-fill tank. Emission spectrographic analyses indicated that the concentration of chromium in the salt had increased from less than 0.001 w/o to 0.01 w/o. During a period of continuous operation the oxygen content of the salt decreased slowly, and between the first and second run, the oxygen content decreased from about 0.3 w/o to 0.1 w/o and remained at the lower level through the third run. The concentrations of other impurities (iron and nickel) were all below the level of detection.

3. Materials Testing (M. L. KYLE, L. F. DORSEY, J. ARNTZEN, A. RASHINSKAS)

Liquid Cu-Mg, Zn-Mg, and Cd-Zn-Mg alloys in combination with molten chloride salts are being investigated as potential solvent systems for pyrochemical processes. A materials testing program is being conducted to evaluate the suitability of various materials of construction for process applications (see ANL-7125, p. 38). Such items as crucibles, transfer lines, agitators, and associated equipment will be required, and the materials selected for each application may not necessarily be the same. The emphasis is currently placed on liquid Cu-Mg alloys, which are used as donor alloys in salt transport separations, and on com-

mon, easily fabricated materials such as ferrous alloys and graphites. Corrosion rates of various materials are being obtained and, in addition, the effects of different materials on the stability of liquid metal and molten salt solutions of uranium are being studied. Although an acceptable corrosion rate is an essential requirement for the process equipment, it is also necessary to avoid losses of uranium and plutonium resulting from interactions with the process equipment. Even minor reactions of the uranium or plutonium solute could cause significant losses and thereby seriously affect their recovery in a process.

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FIG. I-15. Stability of Cu-Mg-U/Salt Systems in Cast Iron.

Run:	A	B
Symbol:	○	●
Time:	216 hr	192 hr
Temperature:	850°C	850°C
Metal Phase:		
Weight:	2,426 g	2,065 g
Composition:	88 w/o Cu- 9.7 w/o Mg- 2 w/o U	88 w/o Cu- 9.7 w/o Mg- 2 w/o U
Salt Phase:		
Weight:	390 g	500 g
Composition:	50 m/o MgCl ₂ - 30 m/o NaCl- 20 m/o KCl	100% MgCl ₂

a. CONTAINMENT OF Cu-Mg-U/HALIDE SALT SYSTEMS

Corrosion Resistance of Cast Iron to Cu-Mg-U/Salt Systems. Cast iron appears to be a potential container material for Cu-Mg-U/halide salt systems and is currently being tested for this application. Six crucibles (4½-in. OD by 6½ in. high by ¼-in. thick wall cast with four integral mixing baffles about ⅝ in. wide and extending ⅞ in. into the crucible) have been obtained and, to date, two have been tested.

One cast iron crucible was exposed to a Cu-9.7 w/o Mg-2 w/o U/50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl¹² salt system for 170 hr at 800°C and 216 hr at

¹² This system is one of several being investigated for the reduction step.

850°C (386 hr total) with no corrosion visually evident. This crucible was sacrificed for metallographic examination, which revealed no detectable corrosion except for the formation of a metal surface film about 5 to 15 mils thick. This film appeared to be primarily a Cu-Mg-U metal phase adhering to the wall, but the possibility exists that the material contains uranium carbide or an iron-uranium intermetallic compound. Samples have been submitted for electron microprobe and X-ray diffraction analyses, and these results will be presented in a subsequent report.

The second crucible was exposed to a Cu-9.7 w/o Mg-2 w/o U/MgCl₂ salt system for 192 hr at 850°C. The change in the salt phase from MgCl₂-NaCl-KCl to pure MgCl₂ and the increase in temperature to 850°C result in a system and conditions that approximate those expected in the flowsheet. Visual examination of this crucible again indicated no evidence of serious corrosion.

To determine the stability of the solute uranium, uranium analyses were performed on samples taken during the runs. In the 170-hr run only initial and final samples were taken for uranium analyses, since the corrosion resistance of cast iron to the process solutions was unknown. In this run, the uranium concentration decreased from 1.02 w/o to 0.48 w/o during the 170-hr period, a loss of approximately 12 g of the 23 g of uranium charged. In the 216-hr run with the first crucible and in the run with the second crucible, samples were taken periodically throughout the runs. The results of the uranium analyses for the latter two runs are plotted in Figure I-15.

These results are not considered conclusive, but they appear to suggest that Cu-Mg solutions of uranium in cast iron may be unstable. The apparent solution stability problem appears in all three runs, the amount of uranium lost from solution being approximately 12, 11 and 10 g, respectively. The loss of approximately 12 g of uranium during the first use of the crucible and the 11-g loss during reuse of the same crucible indicate that the phenomenon causing the uranium loss from solution may occur during repeated use of the same crucible. These losses are equivalent to about 0.02 g of uranium/cm² of crucible surface area and may be acceptable for some applications, especially if some of this loss can be recovered or if the loss can be diminished by repeated use of the same crucible. The mechanism may involve the formation of a surface film which is normally adherent but which is ruptured during thermal cycling of the crucible. In an application in which the crucible would be held at temperature between runs, the uranium loss might be acceptably low. These results are not considered to be conclusive evidence for removing cast iron from the list

of possible container materials for Cu-Mg-U alloys. Further testing will be performed in an effort to understand more fully the mechanism of uranium loss, since it may be possible to decrease it to an acceptable level.

Similar tests are being conducted with CB-30 cast steel, which has a low carbon content (0.17 w/o compared with 3.48 w/o carbon for the cast iron used in these tests), to determine if the carbon content of the steel is a contributing factor to the uranium loss and whether this loss can therefore be avoided by the use of low-carbon steels.

Corrosion of Croloy 16-1¹³ by Cu-Mg-U/Salt Systems. Croloy 16-1 is a ferritic stainless steel that is available as both tubing and pipe. This alloy is similar in chemical composition to type 405 stainless steel¹⁴ which is not readily available in fabricated forms. Because of favorable experience in the containment of many molten metal/salt systems by type 405 stainless steel, Croloy 16-1 is currently being tested for possible utilization as a process transfer line material for molten Cu-Mg/salt systems. Croloy 16-1 was exposed to a Cu-9.7 w/o Mg-2 w/o U/50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl system for 197 hr at 800°C. A second run was conducted under similar conditions except that the temperature was raised from 800 to 850°C and MgCl₂ was used as the salt phase rather than the MgCl₂-NaCl-KCl mixture. The results of the two runs are compared in Table I-2. In both runs the material was exposed as agitator blades affixed to a Mo-30 w/o W alloy agitator shaft. The blades were located on the shaft so as to expose one blade to the metal phase, one to the metal/salt interface, one to the salt phase, and one to the vapor phase.

The corrosion rates observed in the salt and vapor phases were roughly the same in the two runs (~1 to 4 mils). Metal phase and interface corrosion were much more severe in localized areas in the run performed at 850°C with the MgCl₂ salt. In this run, certain areas of the agitator blades exposed to the metal phase and metal/salt interface were attacked to depths up to about 100 and 50 mils in 191 hr, respectively. These high corrosion rates were observed only in localized areas. The remainder of the blades evidenced corrosion rates similar to those reported previously (ANL-7125, p. 38).

The areas of severe localized corrosion were located on opposite sides at opposite ends of the blades. This result suggests that fluid dynamics played an important role in the corrosion. Metallographic examination in-

TABLE I-2. CORROSION OF CROLOY 16-1 IN Cu-Mg-U/SALT SYSTEM

	Run	
	CuMg-3	CuMg-11
Temperature	800°C	850°C
Exposure time	197 hr	191 hr
Crucible (2400 ml)	Al ₂ O ₃	Al ₂ O ₃
<i>Metal phase</i>		
Weight	5880 g	3330 g
Composition	Cu-9.7 w/o Mg-2 w/o U	Cu-9.7 w/o Mg-2 w/o U
<i>Salt phase</i>		
Weight	820 g	500 g
Composition	MgCl ₂ -30 m/o NaCl-20 m/o KCl	MgCl ₂
Agitator speed ^a	435 rpm	200 rpm
<i>Observed Depth of Corrosion^b (mils)</i>		
Metal phase	4-16	2-10 ^c , 100 ^d
Metal-salt interface	6	2-7 ^c , 50 ^d
Salt phase	0.5	1
Vapor phase	2	4

^a In both runs the samples were exposed as four agitator blades affixed to a Mo-30 w/o W shaft.

^b Agitator blade, 0.120 in. thick by 3/8 in. wide by 2 3/8 in. long.

^c Generally observed.

^d In localized areas.

indicated that the mode of attack is by the formation of a surface reaction film. (A sample of this film is currently awaiting electron microprobe analysis.) If this film is normally protective but can be removed by the mechanical action of the fluid over the surface, one would expect the type of corrosion that was observed. The reason for the occurrence of this phenomenon in the metal phase in Run CuMg-11 and not in Run CuMg-3 is not known. It is hoped that analysis of the surface film will aid in the interpretation of the mechanism of corrosion in this system.

An additional test was performed to determine if Croloy 16-1 is susceptible to stress corrosion cracking by the MgCl₂ salt phase. In this test a piece of this alloy was deliberately highly stressed by a 90° bend over a small bend radius (about 0.020-in. radius for a 0.120-in. thick specimen). This piece was contacted with MgCl₂ (dried by melting and contacting with molten magnesium) at 850°C for about 70 hr. Examination of this specimen after exposure indicated no evidence of ordinary corrosive attack or of stress corrosion cracking.

The significance of these corrosion rates cannot be fully assessed until more information is available on the compound formed by the reaction. It may be possible to avoid the formation of the reaction layer by

¹³ Chemical composition: 15 w/o Cr, 1 w/o Ni, 1 w/o Mn, balance Fe and minor constituents.

¹⁴ Chemical composition: 13 w/o Cr, 1 w/o Mn, 0.2 w/o Al, balance Fe and minor constituents.

TABLE I-3. CORROSION OF VITREOUS CARBON BY MOLTEN METAL/SALT SYSTEMS
Temperature: 800°C

Run	Crucible ^a	Duration (hr)	Metal Phase	Salt Phase	Remarks
Zn-U or Zn-Mg-U/Salt Systems					
SRP-0	A	24	Zn-5 w/o Mg-10 w/o U	^b	No wetting, crucible fractured for examination
2	B	151	Zn-2 w/o U	^b	No wetting
3	B	200	Zn-5 w/o Mg-2 w/o U	^b	No wetting
4	B	210	Zn-2 w/o U	^b	No wetting, crucible failure in handling
5	C	208	Zn-2 w/o U	^b	No wetting
6	C	209	Zn-2 w/o U	^c	Slight wetting (10% of crucible surface)
9	C	238	Zn-2 w/o U	^c	Slight wetting (~50% of crucible surface)
Cu-Mg-U/Salt Systems					
CuMg-4	D	210	Cu-10 w/o Mg-2 w/o U	^c	No wetting
5	D	111	Cu-10 w/o Mg-2 w/o U	^c	No wetting

^a Four identical 1½-in. dia. crucibles were used.

^b Salt composition: 47.5 m/o MgCl₂-47.5 m/o CaCl₂-5 m/o MgF₂.

^c Salt composition: 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl.

variations in process temperature or solvent composition. Even for the conditions used in this run, a corrosion rate of 14 to 16 mils/200 hr may be acceptable for transfer lines and other items of process equipment such as agitators, thermocouples wells, and samplers, if the severe localized corrosion can be eliminated.

Corrosion of Vitreous Carbon by Molten Metal/Salt Systems. Corrosion testing of vitreous carbon in Zn-U/salt, Zn-Mg-U/salt, and Cu-Mg-U/salt systems is continuing (see ANL-7125, p. 39). A summary of all tests completed to date is given in Table I-3. As indicated in the table, this material appears resistant to both systems at 800°C. Wetting of the crucible in a Zn-2 w/o U/salt system did not take place until after 417 hr of exposure. This wetting was slight, covering about 10% of the crucible surface that was exposed to the system, and it did not prevent easy mechanical removal of the charge. A total exposure time of 655 hr increased the amount of wetting to 50% of the available surface but again did not cause sticking of the charge. Exposure to the Cu-10 w/o Mg-2 w/o U system for a total of 321 hr resulted in no wetting of the crucible surface. It is concluded that vitreous carbon may be an excellent container material for these systems, and larger crucibles (4-in. OD by 7 in. high) are now being obtained.

b. CONTAINMENT OF Zn-Mg-U/HALIDE SALT SYSTEMS

Corrosion of W-0.1 w/o Ni in Zinc/Salt Systems. The addition of approximately 0.1 w/o nickel to the

tungsten powder used in fabricating finished tungsten shapes by the pressing-and-sintering technique is apparently useful in decreasing the interconnected porosity present in the finished piece. The formation of a W-Ni solid solution alloy during the sintering process is believed to produce improved bonding of the structure.

In a previously reported test (ANL-7125, p. 38) tungsten containing 0.1 w/o nickel was unaffected by a zinc/47.5 m/o MgCl₂-47.5 m/o CaCl₂-5 m/o MgF₂ salt system at 800°C after 200 hr exposure. Two additional samples of the W-Ni material were obtained from the Y-12 plant at Oak Ridge National Laboratory and tested for corrosion resistance to a zinc/MgCl₂-30 m/o NaCl-20 m/o KCl salt system. The W-Ni samples were tested as agitator blades at 325 rpm in the two-phase system. Four coupons, two made from each sample, were tested for 380 hr at 800°C. Examination of these samples after exposure indicated no appreciable corrosion (<0.2 mil) or structure change during exposure.

It is concluded that this material is corrosion resistant to zinc/salt systems.

Corrosion of Pyrolytic Boron Nitride by Zn-Mg/Salt Systems. Pyrolytic boron nitride was tested as a candidate material for process application. This material is produced by a vapor deposition process; BCl₃ and NH₃ are reacted to form boron nitride which is vapor deposited on the substrate. The interest in this material stems primarily from the fact that it can be deposited in thin layers on graphite to provide a coating that is impervious to gases. A 2- to 5-mil coating of

this material deposited on a graphite crucible (2-in. OD by 3 in. high) was tested in a Zn-5 w/o Mg-2 w/o U/MgCl₂-30 m/o NaCl-20 m/o KCl salt system at 800°C for about 400 hr. At the end of this time, the crucible was sound with no evidence of salt or metal leakage. Further testing of this material may be conducted when larger size crucibles are available.

c. CONTAINMENT OF MOLTEN METAL/SALT SYSTEMS IN CONVENTIONAL GRAPHITE AND SILICON CARBIDE

Conventional grades of graphite are being reexamined for the containment of process solutions. These materials have not been used recently because tests performed several years ago indicated that graphite was porous to molten salts and that the formation of uranium carbide resulted in uranium losses. Recent advances in the quality and density of the available forms of graphite, along with the development of spray coatings and pretreatment processes for rendering graphite usable for uranium solutions, have led to a renewed interest in the use of graphite.

Three commercial grades of graphite—ATJ ($\rho = 1.73$ g/cc),¹⁵ CGW ($\rho = 1.80$ g/cc), and ZTA ($\rho = 1.95$ g/cc)—were fabricated into small crucibles (1½ in. OD by 1⅞ in. high by ⅝ in. wall) and subjected to a zinc-uranium/MgCl₂-30 m/o NaCl-20 m/o KCl salt system for approximately 100 hr at 800°C. These tests were designed to determine if the molten salt phase would seep through the thin (<¼ in.) crucible wall. No attempt was made to determine the stability of a uranium solution. In all cases the solutions were successfully contained and no seepage of salt occurred. Sectioning of the wall of the type ATJ graphite crucible revealed no penetration of the salt phase into the crucible wall. Larger graphite crucibles are being obtained for further testing.

Silicon carbide has also been considered as a possible crucible material for pyrochemical processes. This material is relatively inexpensive, easily available, and apparently inert to process solutions. It has been unusable for process applications, however, since the density of the finished product was too low to contain the molten salts, which readily seeped through the crucible wall.

The Carborundum Corporation is currently attempting to develop high-density forms of silicon carbide. A small sample crucible (¾-in. ID by 2 in. long) was supplied to use for test purposes. This crucible successfully contained molten MgCl₂ in a 24-hr test at 300°C with no apparent leakage. Larger size crucibles of this material have been ordered for testing.

d. CORROSION OF FERROUS ALLOYS AND TANTALUM BY Al-Mg/SALT SYSTEMS

The potential usefulness of Al-Mg alloys as solvents for use in the disposal of radioactive wastes containing fission product yttrium and rare earths has led to a study of the corrosion resistance of various materials of construction to Al-Mg/MgCl₂-30 m/o NaCl-20 m/o KCl salt systems (ANL-6925, p. 36).

Four ferrous alloys (1020 carbon steel, type 4130 chrome steel, types 304 and 405 stainless steels) were exposed to 60–90 w/o Al-Mg/salt systems for 400 hr each at temperatures of 500 and 800°C. In these tests 5 w/o cerium was added to the metal phase to simulate the rare earth content in the proposed application. Each metal coupon and its solvent medium was sealed in a tantalum capsule. The loaded capsules were rotated end-over-end.

The Al-Mg/salt system is highly corrosive to ferrous alloys. At 800°C all samples subjected to the environment were completely destroyed. At 500°C, all samples except the type 304 stainless steel (<1 mil/400 hr) were severely corroded at aluminum concentrations below 90 w/o. It is concluded that ferrous alloys are not suitable container materials for Al-Mg/salt systems.

The tantalum capsules that had contained the corrosion test specimens were examined in all cases where severe corrosion of the ferrous alloy occurred. At 500°C all liquid metal compositions tested produced very little corrosion (0.5 mil/400 hr) of the tantalum capsule. At 800°C, however, definite corrosion was observed and appeared to increase with increasing aluminum content of the metal phase. At ~90 w/o aluminum, the corrosion rate was estimated to be 3 mils/400-hr exposure. A surface reaction layer that appeared to be an intermetallic compound (possibly TaAl₃) was observed on many of the samples exposed at 800°C. The layer, which in some cases reached a depth of about 3 mils, appeared to be adherent and relatively dense. It is concluded that tantalum also may not be a suitable containment material for extended service in this system when alloys with high aluminum contents are present.

e. OXIDATION RATE OF TENELON¹⁶ STEEL

Tenelon steel is typical of a relatively new class of steel alloys now in production. These alloys are austenitic in structure (as is type 304) but do not contain an appreciable amount of nickel. (Nickel has a relatively high solubility in the solvent metals of interest.) Because of their austenitic structure the materials possess excellent high temperature properties

¹⁵ Theoretical density of graphite, $\rho = 2.25$ g/cc.

¹⁶ Product of United States Steel Corporation.

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FIG. I-16. Oxidation Rate of Tenelon Steel in Air.
Temperature: 800°C
Symbols denote individual samples.

(5600 psi stress-rupture strength at 825°C as compared with 3700 psi for type 304), good weldability, and relative ease of fabrication. These alloys are currently being evaluated for possible use in pyrochemical processes.

A test has been conducted to determine the air oxidation resistance of Tenelon steel at the temperatures of interest. This test was conducted at 800°C for a total air exposure time of 1000 hr. Results are pre-

sented in Figure I-16. The results indicate that Tenelon produces a protective oxide coating, as do the 18-8 stainless steels, with the result that the oxidation rate decreases sharply with increasing exposure times. Tenelon should be usable in air at 800°C for periods of time well in excess of 1000 hr. The amount of scale formed after 1000 hr corresponds roughly to a 1- to 2-mil loss of the original surface.

f. CORROSION RESISTANCE OF SHEAR-FORMED TUNGSTEN CRUCIBLE TO PROCESS CONDITIONS

The shear-formed tungsten crucible (11-in. OD by 18.1 in. high by 0.18-in. wall) fabricated by Metallwerk Plansee (Austria) (ANL-7125, p. 39) is being tested for possible process application. The empty crucible was initially tested by thermal cycling in an argon atmosphere for a total of 15 cycles between 600 and 800°C. Since no noticeable deterioration occurred, this crucible was used as the container for the Zn-Mg-U/MgCl₂ system employed as the acceptor alloy in the first exploratory run on the salt transport process and for the Cu-Mg-U/MgCl₂ system used as the donor alloy in the subsequent runs (see Section B-1). During these runs the crucible was exposed to the Zn-Mg-U/salt and Cu-Mg-U/salt for a total of about 130 hr during the runs and subsequent product washes. This crucible was subsequently cleaned with acid and appeared to be in excellent condition. The crucible will continue to be used in salt transport process development and will be inspected after each run.

It appears that the shear-forming method of crucible fabrication produces the sound, lightweight crucible that was anticipated.

C. PROCESS EQUIPMENT DEVELOPMENT—SKULL RECLAMATION PROCESS (G. J. BERNSTEIN, R. K. STEUNENBERG, P. FINEMAN)

At the conclusion of the EBR-II melt refining operation, a residue (skull) remains in the processing crucible. A process is being developed for reclaiming the fuel material from the skull and removing fission products from the recovered fuel material. The recovered material is then returned to the melt refining process as make-up material. The skull is initially converted into a free-flowing oxide powder in a skull oxidation furnace, which is now in use in the EBR-II Fuel Cycle Facility (see ANL-6900, pp. 116, 118-120). Plant-size equipment for processing the skull oxides in the Fuel Cycle Facility has been built and tested

by this Division. The equipment is sized for operation on about 5.8 kg of skull oxide (~5 kg of uranium oxide), which is equivalent to the amount of skull material produced in about seven normal melt refining skulls.

The skull reclamation process consists of the following operations. (1) The oxidized skull material is charged to a molten halide salt flux, the salt phase is contacted with liquid zinc to extract the noble metals, fission products, and the zinc phase is removed. (2) The salt phase is then contacted with a magnesium-

rich Zn-Mg alloy which reduces the uranium oxides to metal. Metallic uranium, which has a very low solubility in the Zn-Mg alloy, precipitates from solution. The salt and the supernatant alloy, which contain the remaining fission products, are transferred off as wastes. (3) The uranium product is redissolved in a zinc-rich Zn-Mg alloy and the solution is transferred to a mold. (4) The resulting U-Zn-Mg ingot is retorted

to remove zinc and magnesium and the metallic uranium product is consolidated by melting.

Two furnaces are required for the process: (1) a reduction furnace where the noble metal extraction, oxide reduction, and uranium redissolution steps are performed, and (2) a retorting furnace where solvent metals are vaporized from the uranium and the uranium sponge is melted.

1. Reduction of Skull Oxide to Uranium Metal (D. E. GROSVENOR, W. E. MILLER, J. WOLKOFF, R. C. PAUL, P. J. MACK, A. L. CHANDLER, P. KELSHEIMER,¹⁷ E. F. JOHNSTON)

a. FIRST SERIES OF REDUCTION FURNACE RUNS

In the preceding semiannual report (ANL-7125, pp. 44-45) results of three runs (SRR-2, -3, and -4) of the first series of ten test runs were discussed. These results indicated that reaction conditions were not sufficiently vigorous to produce the desired degree of uranium oxide reduction or noble metal fission product removal. Similar results were obtained in runs SRR-5, -6, and -7, in which the operating conditions were varied only slightly from the conditions of the earlier runs.

In runs SRR-8, -9, -10, changes were introduced in the composition of the salt flux. (The salt composition in the preceding runs was 47.5 m/o MgCl_2 -47.5 m/o CaCl_2 -5 m/o CaF_2 .) In runs SRR-8 and SRR-9 50 m/o MgCl_2 -50 m/o CaCl_2 was used. In SRR-10, the salt composition was 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl . These changes were made to avoid the carryover of Ca^{++} and F^- ions in the small amount of flux which is transferred with the final U-Zn-Mg solution produced in the reduction furnace. (The fabricator of the beryllia crucible that is used in the retorting operation had indicated that Ca^{++} and F^- ions were deleterious to the crucible.) In the absence of fluoride ion, the removals of molybdenum, ruthenium and zirconium as determined by product solution analyses appeared to be significantly enhanced (80-90% removal *vs.* ~50% removal). However, the absence of fluoride in the salt mixtures resulted in high uranium losses (~14%) in the waste salt from the reduction step, thereby indicating that fluoride ion is necessary for achieving high reduction of uranium oxide. The effect of fluoride ion upon uranium oxide reduction and fission product removal was investigated further in a second set of test runs described in a subsequent section (subsection c). Traps of alumina-silica were also tested in this series as a

means of removing the small amount of flux that is carried over with the final U-Zn-Mg solution.

b. REDUCTION FURNACE INSPECTION

Following the completion of the series of ten skull reclamation runs (SRR-1 through SRR-10) in the plant-scale reduction furnace (see ANL-7125, p. 44) the inert-atmosphere enclosure in which the equipment was located was returned to an air atmosphere. The reduction furnace was disassembled to permit direct inspection of its interior and auxiliary components (see ANL-7055, pp. 62-66). The interior heat shields and insulator assembly were coated with about 4 kg of granular and dusty metal deposits, presumably from condensed zinc and magnesium vapors. The interior of the tungsten crucible was coated with a rough cinder-like material weighing 2.4 kg and consisting principally of UO_2 , MgO , and ZnO . (About 15 w/o was uranium.) The metal heel in the crucible weighed 703 g and was approximately 10 w/o U, 12 w/o Mg, and the balance zinc.

The Hastelloy C furnace body was in excellent condition; no corrosion was apparent and only traces of zinc and flux dust were found in the larger, upper section of the furnace body.

The agitator assembly was removed and disassembled to permit examination of the bearings, packing, shaft, and impeller (see ANL-6925, p. 60 for equivalent test assembly). The top ball bearing which had been lubricated with radiation-resistant grease (NRRG-159)¹⁸ was in good condition and was reused without regreasing. The graphitar¹⁹ bearing above the packing showed approximately 0.005 in. of wear, but was in good condition. The MoS_2 -lubricated packing rings were pliable and reusable. The bottom graphitar annular ring functioned as a steady bearing and was in good condition. During the operation of the furnace,

¹⁸ Product of Standard Oil Company of California.

¹⁹ TS574 carbon: Product of National Carbon Company, Division of Union Carbide Corp., New York, New York.

¹⁷ Design Group.

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FIG. I-17. Operating Conditions for Plant-Scale Skull Oxide Reduction Runs.

an argon purge was maintained through a distributor ring near the bottom of the assembly to prevent the entrance of fumes into the assembly. No corrosion of the shaft or impeller was evident.

The cast iron gear mounted on the mixer shaft and the steel gear mounted on the motor shaft showed considerable wear. These gears had been lubricated initially with dry molybdenum disulfide. New identical gears were installed which were lubricated with APL²⁰ grease to which MoS₂ powder had been added. After eight additional runs no wear was noticeable.

c. SECOND SERIES OF REDUCTION FURNACE RUNS

In order to improve the reaction conditions within the reduction furnace, a second impeller, positioned 1½ in. above the lower impeller and also pitched to discharge downward, was added to the mixer shaft. A three-bar vertical baffle assembly made of Mo-30 w/o W alloy was installed in the tungsten crucible. In addition, operating conditions were changed to provide for higher mixing speeds, higher temperatures and longer duration of the process steps. These conditions are shown in the flow sheet presented in Figure I-17.

Under these conditions a second series of test runs was made. The objectives of the tests were (1) to check mechanical performance of the equipment, (2)

to study the performance of three different MgCl₂-based salt fluxes, and (3) to determine the effect of fluoride ion in the flux upon the removal of fission products and reduction of uranium oxide.

Operation of the reduction furnace continued to be reliable and reproducible. Several modifications in equipment and operating procedures were introduced during the second set of runs. Equipment was added to complete the work on the control of fuming at the furnace and transfer receiver (see ANL-7125, pp. 49-50).

A filter-exhauster assembly has been built and used to remove fumes which appear both at the furnace charging port and at the transfer receiver (see ANL-6925, pp. 61-62, ANL-7055, Figure I-30 and ANL-7125, p. 49). The exhauster is a centrifugal blower which draws the fumes through a set of four Cambridge, Model IF-50 metal-frame, high-temperature, high-efficiency filters. Flexible metal hoses connect the filter unit to the furnace charging port and the transfer receiver. Initial tests of the filter assembly in runs SRR-12, -13, and -14 were made before the ball valve was installed in the charging hopper. Fumes that formed at the charging port were collected by the manifold ring described in ANL-7125, pp. 49-50. Under these conditions 474 g of condensed fumes were collected on the filters and about 500 g of loose material was found in the manifold ring and in the 3-in. duct connecting the manifold ring to the filter assembly. Control of fuming at the charge port and at the transfer receiver was still marginal despite the heavy accumulation on the filters. By far the greater source of fumes collected in the filter was the open charging port. The charge port was open for about an hour during each of these tests; fuming at the transfer receiver took place for only a few minutes during each run. The use of a ball valve charging hopper (described below) will markedly reduce the quantity of material reaching the filter and it is anticipated that a filter of the same capacity as the test filter would remain operable for about 100 runs. A filter cannister suitable for remote handling in the Fuel Cycle Facility has been designed.

A new furnace charging hopper was built which has a 4-in. ball valve as a bottom closure (see Figure I-18). This hopper is permanently attached to the furnace and is opened only to discharge a previously loaded batch of reagents. Experience with this hopper has shown that the ball valve is essentially leak-tight when the furnace is pressurized for transfer of molten materials. The use of this charging hopper has not only eliminated fuming at the charging port but has also simplified the charging operation and reduced the time spent for intermediate charging steps from one

²⁰ Product of Shell Development Company, California.

108-9428

FIG. I-18. Reduction Furnace Charging Hopper with Ball Valve Closure.

hour to a few minutes. A design for incorporating the new charging hopper in the reduction furnace for use in the EBR-II Fuel Cycle Facility has been completed.

Another operating change introduced during the past series of runs was the use of a simple, cup-shaped

strainer or trap to remove the small amount of flux which is transferred with the U-Zn-Mg product from the reduction furnace. The trap is made of alumina-silica fiber and rests on top of the graphite mold in which transferred metal is collected. The molten metal

TABLE I-4. SUMMARY OF PLANT-SCALE SKULL OXIDE RECLAMATION RUNS SRR-11 THROUGH SRR-18

Run	Flux ^a	Fluoride Salt		% U ^d Unreduced	% of Charge in Discharged Product Solution ^e					% of Charge in Retorted Product U ^g
		m/o F ^b	Time of addition ^c		U ^f	Mo	Ru	Ce	Zr	
11	B	None	—	7.8	81.1 (84.1)	27	10	5	23	85.4
12	B	2	R	3.8	96.9	28	16	4	30	94.1
13	A	10	R	1.4	91.6	31	16	3	34	92.4
14	A	10	R	1.0	95.2	34	15	2	41	93.9
15	B	10	N	0.7	88.5 (93.2)	67	20	3	27	84.8
16	B	10	N	0.9	86.6 (87.4)	64	16	3	55	85.3
17	C	10	N	0.7	90.9	29	19	3	46	103.7
18	C	10	R	2.3	84.4	27	12	2	26	79.0
Overall Averages					89.4 (90.5)	38	16	3	35	89.8

^a Flux compositions: A—50 m/o MgCl₂-50 m/o CaCl₂; B— 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl; C—50 m/o MgCl₂-50 m/o NaCl.

^b Added as NaF except in runs 13 and 14 in which CaF₂ was used.

^c R = fluoride added immediately before reduction step, N = fluoride added before the noble metal extraction step.

^d Determined by chemical analysis of samples of the waste flux after reduction.

^e Determined by chemical analysis of dip samples of the product solution before transfer to the product mold.

^f Numbers in parentheses are values corrected for the amount of heel remaining in the crucible. Run 15 includes a correction for losses in a plugged transfer line.

^g Uranium content of the retorted product determined by difference based on chemical analyses for Mo, Ru, Ce, and Zr.

drains through holes in the bottom of the trap while the flux preferentially wets the body of the trap and is retained. The trap must be degassed under vacuum at about 800°C to remove residual moisture which would otherwise react with the molten metal. The use of these traps has eliminated contamination of product solutions by flux and subsequent difficulties with Ca⁺⁺ or F⁻ in the BeO retorting crucible.

No further process testing in this equipment is planned. The skull reclamation process has been successfully demonstrated. The installation of the skull oxide reduction furnace and the retorting furnace (discussed below) in the Fuel Cycle Facility, however, has been postponed.

The results of the eight-run series are summarized in Table I-4. In general, the three fluxes tested performed equally well with respect to uranium reduction and fission product removals. The primary factor in achieving high uranium reduction was the presence of about 10 m/o fluoride ion, which is seen by comparing the results of runs SRR-11 and -12 with those of subsequent runs.

The effect of fluoride ion in the noble metal extraction step upon removal of molybdenum and ruthenium is not clearly defined. In two runs, SRR-15 and SRR-16 where 10 m/o fluoride ion was present in the noble metal extraction step, analyses of the product solutions showed only about 35% removal of molybdenum. In

runs SRR-13, -14, and -18 in which fluoride ion was not present in the salt during the noble metal extraction step, approximately 70% removal of molybdenum was found. However, in SRR-17 where fluoride ion (10 m/o) was present in the noble metal extraction step, removal of molybdenum was also about 70%.²¹ Removals of ruthenium were 80 to 90%. Although ruthenium removals in the absence of fluoride salt in the noble metal extraction step were slightly better than in the presence of fluoride, the differences are not considered significant.

Removals of cerium, a representative rare earth, were consistently high, about 97%. Removals of zirconium showed a considerable range, varying from 45% to 77%. However, the average removal of 65% is considered quite adequate for the process.

Recovery of uranium in the product solution varied from 81 to 97% based upon analysis of product solution samples. In runs SRR-15, -16, and -18, uranium recoveries were low because of operational errors which

²¹ In the earlier runs SRR-8, -9, and -10, molybdenum removals appeared to be 80 to 90%. In those runs product solution samples were taken after settling periods of 30 to 60 min in order to improve molybdenum removal. However, this technique did not prove satisfactory, since the settled molybdenum would largely transfer with the product solution. In runs subsequent to SRR-10, the product solution was sampled and transferred without a settling period in order to provide a more representative sample.

TABLE I-5. SUMMARY OF THREE SELECTED SKULL OXIDE RECLAMATION RUNS
(10 m/o fluoride ion present in flux)

Run	% U Reduced	% of Charge in Discharged Product Solution				
		U	Mo	Ru	Ce	Zr
SRR-13	98.6	91.6	31	16	3	34
SRR-14	99.0	95.2	34	15	2	41
SRR-17	99.3	90.9	29	19	3	46
Average	99.0	92.6	31	17	3	40

led to high uranium losses in intermediate process waste streams. The results of runs SRR-13, -14, and -17 are summarized in Table I-5. These runs were made under conditions which closely followed the flow-sheet and are considered to be reproducible. The average uranium recovery of 92.6%, although less than the 95% initially specified for the process, is adequate. Pouring yields for the melt refining process in the EBR-II Fuel Cycle Facility have averaged about 93%. Consequently, a recovery greater than 90% in the skull reclamation process would provide an overall uranium recovery exceeding 99%. Furthermore, there is an accumulation of uranium oxide on the crucible wall (in addition to the product heel) which is recoverable. This accumulation may represent about 1 or 2% of the material charged in each run; the exact amount will be determined when the furnace is opened for examination.

2. Recovery of Uranium Product by Retorting (J. F. LENC, W. E. MILLER, J. WOLKOFF, M. A. SLAWECKI,¹⁷ A. L. CHANDLER, R. C. PAUL, P. KELSHEIMER,¹⁷ E. F. JOHNSTON)

The final process stream from the reduction furnace is about 8 liters of a Zn-12 w/o Mg-12 w/o U solution, weighing approximately 36 kg and containing about 4 kg of uranium. Work is in progress on the recovery of uranium from this solution in a form suitable for use as a supplementary feed material for the melt refining process. Retorting equipment is being developed to recover the uranium by distilling off the zinc and magnesium. To date, development of this retorting equipment has been directed specifically toward the recovery of uranium in the reprocessing of EBR-II fuel. However, a similar procedure may be required in other liquid metal fuel reprocessing schemes currently under consideration. A drawing of the plant-scale (4 to 4.5 kg U) retorting equipment, which was previously presented in ANL-7125, as Figure I-19, is included here for reference as Figure I-19.

The following general conclusions can be drawn from the second series of runs:

a. A total of 32.5 kg of uranium was charged to the process as skull oxide, and of this 89.4% was recovered in the final product solution and 87.8% was recovered as retorted product. These recoveries are average values that include results from runs conducted under both favorable and unfavorable operating conditions.

b. A uranium recovery of 92.6% (equivalent to about 99% overall recovery for the melt refining and skull reclamation processes) in the product solution was typical of runs performed under favorable operating conditions.

c. The presence of 10 m/o fluoride ion in the salt flux was beneficial to uranium reduction, and with it uranium reductions of 99% can be achieved routinely. Without fluoride, the uranium reduction yield decreased to 92%.

d. The three fluxes tested were nearly equivalent relative to uranium reducibility.

e. There appeared to be no significant effect of fluoride in the salt on ruthenium removal in the noble metal extraction step, but it appeared to inhibit molybdenum removal.

f. Removals of the fission product elements molybdenum, ruthenium, cerium, and zirconium were adequate for the EBR-II fuel cycle.

g. The present plant-scale skull reclamation process equipment has operated reliably and reproducibly.

a. PLANT-SCALE RETORTING EQUIPMENT

During the last six months, nineteen additional runs (PSR-7 through PSR-25) were completed in the plant-scale retorting unit located in the large argon-atmosphere enclosure. Pertinent distillation data from these runs are listed in Table I-6. The nominal composition of the charge material was Zn-12 w/o Mg-5 to 12 w/o U. A typical retorting charge ingot is shown in Figure I-20. All runs were conducted at a nominal pressure of 10 torr in a thixotropically cast beryllia crucible. The bulk of the volatile zinc and magnesium metal present in the charge was distilled at temperatures of 650 to 750°C. Vaporization of the remaining volatile material and liquation of the uranium product were achieved by increasing the temperature to 1150–1200°C for about 45 min.

Containment of the distillate vapors within the

FIG. I-19. EBR-II Retorting Equipment.

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graphite enclosure of the retort assembly (see Figure I-19) was satisfactory in all of the recent runs except two (PSR-8 and -9). A material balance for the metal distilled in the seventeen satisfactory runs is shown in Table I-7. The amount of distillate that escaped from the graphite enclosure is equal to the sum of the metal condensed on the Fiberfrax insulating sleeve and the material unaccounted for. As shown in Table I-7, only about 0.6 w/o of the distillate condensed on the Fiberfrax sleeve and only about 0.3 w/o of the distillate was unaccounted for.

In the remaining two runs (PSR-8 and -9), highly turbulent boiling of the U-Zn-Mg retorting solution occurred. In both runs, the condenser was unseated from the collector (see Figure I-19), thereby allowing an appreciable amount of the distillate vapors to escape from the graphite enclosure. About 13 w/o of the distillate condensed on the Fiberfrax insulating sleeve and about 5 w/o was unaccounted for. The highly tur-

bulent boiling (and the resulting high rate of distillation) is attributed to the fact that the power was increased during the initial 2 to 3 hr of distillation. In all of the other runs, the power input to the retort induction furnace was maintained at a constant value for the first 2 to 3 hr.

On the basis of experience gained to date, it appears that large changes in the temperature and pressure of the melt should be avoided during the first few hours of distillation.

The total weight of retorted uranium product and the weight of retorted product recovered for each of the nineteen recent runs are listed in Table I-6. Since a crucible is reused without completely removing small amounts of the product which cling to the crucible wall, in some runs the quantity of uranium product which is removed as an ingot may be slightly greater than the weight of retorted product. The bulk of the retorted product in all of these runs was in the form

TABLE I-6. DISTILLATION RUNS CONDUCTED IN PLANT-SCALE RETORTING APPARATUS^a

Nominal pressure: 10 torr

Distillation temperature: 650–750°C, increased to 1150–1200°C for final 45 min.

Retorting Run No.	Retorting Charge from Reduction Furnace Run No.	Weight of Retorting Charge ^b (kg)	Apparent Distillation Time (min)	Apparent Average Distillation Rate (g/min)	Weight of Uranium in Charge ^c (kg)	Weight of Retorted Uranium Product ^d (kg)	Weight of Uranium Product Ingot Removed ^e (kg)
PSR-7	SRR-9	34.45	568	55	2.89	3.00	2.80
PSR-8	SRR-11	34.30	578	53	3.53	3.80	3.80
PSR-9	SRR-12	34.15	590	51	3.89	3.90	3.92
PSR-10	SRR-13	33.75	708	42	3.64	3.75	3.79
PSR-11	SKR-29 ^f	15.90	414	35	1.56	1.58	1.53
PSR-12	SRR-14	33.35	574	51	3.84	3.90	3.87
PSR-13	SRR-16	33.85	662	46	3.45	3.50	3.44
PSR-14	SRR-17	35.45	716	44	4.08	4.20	3.99
PSR-15	SRR-15	30.60	660	41	3.49	3.45	3.45
PSR-16	SRR-18	34.40	595	52	3.37	3.20	3.30
PSR-17	SKR-25 ^f	15.80	411	35	1.36	1.40	1.44
PSR-18	SRR-10	35.80 ^g	704	47	2.51	2.55	2.57
PSR-19	SRR-2	34.10 ^g	622	50	3.00	3.05	3.11
PSR-20	SRR-1	35.15 ^g	697	47	1.97	2.10	2.13
PSR-21	SRR-3	36.30 ^g	714	46	3.25	3.35	3.53
PSR-22	SKR-21 ^f	13.15	368	33	1.09	1.15	1.26
PSR-23	SKR-19 ^f	12.75	340	35	0.94	0.95	1.02
PSR-24	SKR-27 ^f	15.30	390	36	1.27	1.30	1.30
PSR-25	USTP-3 ^h	36.60	733	46	3.00	3.00	2.78

^a Apparatus sized for full-scale (about 4.0 to 4.5-kg uranium basis) operation in the EBR-II Fuel Cycle Facility in Idaho.^b Nominal composition: Zn-12 w/o Mg-5 to 12 w/o U.^c Based on uranium analysis of the product solution prior to its transfer from the reduction furnace.^d Equals the weight of the BeO retorting crucible and the retorted product after the run, less the weight of the BeO crucible and residual product before the run. Product is essentially uranium with 1 to 2 w/o residual fission product elements.^e Equals the weight of retorted product which was dumped freely out of the BeO crucible after the run.^f Pilot-Scale Skull Reclamation Process Demonstration Run conducted by I. Winsch of Pyrochemical Engineering Group.^g Not all of the product from the dissolution step was charged to retorting in this run.^h Pilot-Scale Uranium Salt Transport Process Run conducted by I. Winsch of Pyrochemical Engineering Group.

of a consolidated ingot. A top view of a typical retorted uranium product ingot is shown in Figure I-21 and a bottom view of the same ingot is shown in Figure I-22. In all of the recent runs except one (PSR-25), the retorted product ingot was dumped out of the beryllia crucible with ease. Moderate mechanical prying was required to free the uranium product ingot from the crucible bottom in run PSR-25.

b. PLANT-SCALE BERYLLIA RETORTING CRUCIBLES

The nineteen recent runs were conducted in four different thixotropically cast (thixocast) beryllia crucibles.²² Six of the runs (PSR-7 through PSR-12) were made in the same thixocast crucible that had been used in four of the previous runs (PSR-1, -2, -3, and -6) described in the preceding semiannual report (ANL-

²² Fabricated by The Brush Beryllium Company of Elmore, Ohio.

7125, p. 50). Figure I-23 shows the condition of the external surface of the crucible after the ten runs. Of the thirteen remaining runs of the recent series, six runs (PSR-13, -15, -17, -18, -19, and -20) were made in a crucible designated BeO No. 1, six runs (PSR-14, -16, -21, -22, -23, and -24) were made in a crucible designated BeO No. 8, and one run (PSR-25) was made in a crucible designated BeO No. 7.

All four of these beryllia retorting crucibles were successful in containing the bulk of the uranium product and are still intact. After each of the nineteen recent runs, however, a small quantity (estimated to be less than 25 g) of uranium was found in the annular space between the beryllia crucible and its graphite secondary container. The presence of uranium in this annulus is attributed to seepage of the Zn-Mg-U retorting solution through the crucible wall.

Arrangements have been made to have The Brush Beryllium Company investigate the significant vari-

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Fig. I-20. Typical Retorting Charge Ingot.
Nominal Composition: Zn-12 w/o Mg-5 to 12 w/o U

ables involved in fabricating high integrity, plant-scale beryllia retorting crucibles. A minimum of twelve plant-scale crucibles are to be supplied to ANL in sets of two or three. Each set of crucibles is expected to display improved properties relative to (1) containment of the molten Zn-Mg-U retorting charge and (2) release of the retorted uranium product ingot.

Thus far, Brush has produced a total of nine plant-scale crucibles. Five of these crucibles (designated BeO Nos. 1, 6, 7, 8, and 9) have been received. The remaining four crucibles (designated BeO Nos. 2, 3, 4, and 5) were rejected by Brush because of various imperfections detected either after casting or after firing. Based on the performance of three of these crucibles (BeO Nos. 1, 7, and 8) tested to date, release of the retorted uranium product ingot is satisfactory. However, improvement is required in the impermeability of the crucibles to molten Zn-Mg-U.

c. DETECTION OF "BUMPING" OR NUCLEATE BOILING DURING RETORTING

Vaporization from the surface of the metal being retorted normally occurs quietly without nucleate boiling, surging, or bumping. These three phenomena, listed in order of increasing violence, result from application of excessive power to the furnace. The phenomena can occur at the start of vaporization when the initial heating rate is too high. Their occurrence is undesirable since the more violent of these can dislodge the condenser-collector assembly, allowing the metal vapor to escape, whereupon attack on the electrical components of the furnace can occur. In addition, the entrainment loss of uranium can be excessive under these conditions.

To detect these turbulent phenomena, two independent sensing devices are used during the retorting runs, a seismic-type vibration pickup and a contact microphone. The output of the vibration pickup is viewed on an oscilloscope screen, while the contact microphone is heard through a loudspeaker. The simultaneous use of these sensors successfully eliminates any ambiguity that results from high background noise in either channel. The combination of the two sensing devices has been in routine use for about six months and has proven to be effective.

The background noise level is high and originates from such sources as building vibration, crane operation, fan operation, and the 10-kc induction power used for heating the retorting furnace. Electrical filtering of the signals was effective in removing the high-

TABLE I-7. MATERIAL BALANCE FOR ZINC-MAGNESIUM VAPORIZED IN SEVENTEEN RUNS (PSR-7 AND PSR-10 THROUGH PSR-25) CONDUCTED IN PLANT-SCALE RETORTING APPARATUS^a

Total weight of volatile metal in seventeen charges: 441.175 kg^b

Location ^c of Volatilized and Condensed Metal	Weight (kg)	Percent of Volatile Metal in Charge (w/o)
In graphite distillate collector	428.675	97.17
On graphite condenser	8.350	1.89
On graphite secondary-container cover	0.075	0.02
On Fiberfrax insulating sleeve	2.800	0.63
Material unaccounted for	1.275	0.29
Totals	441.175	100.00

^a Apparatus sized for full-scale (about 4.0 to 4.5-kg uranium basis) operation in the EBR-II Fuel Cycle Facility in Idaho.

^b Equals the total charge weight (486.700 kg) less the total weight of uranium product (45.525 kg) for the seventeen runs.

^c See Figure I-19, this report.

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FIG. I-21. Top View of Typical Retorted Uranium Product Ingot.

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FIG. I-22. Bottom View of Typical Retorted Uranium Product Ingot.

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FIG. I-23. External View Showing the Condition of a Thixotropically Cast Beryllia Retorting Crucible after Ten Runs.

frequency noise, but could not be used at the lower frequencies where most of the desired signal occurred. A totally enclosed contact microphone is used to minimize atmosphere-borne noises. It is a modification of an Oak Ridge National Laboratory²³ design which uses a carbon button microphone.

The microphone and the vibration pickup are bolted to the outside baseplate of the furnace where they are easily replaced. A 6 $\frac{5}{8}$ -in. dia., lead-shielded housing suitable for manipulator handling contains the vibration pickup and is shown in Figure I-24. The 1-in. square contact microphone housing is shown bolted in position in Figure I-25.

A test to determine the sensitivity of the detection system was made by bubbling argon through a 7-in. deep pool of molten zinc contained in a retorting crucible. It was possible to differentiate by sound between a bubble formed at the bottom and one formed at the top of the pool. Bubbles initiating at the bottom of the pool are more likely to cause bumping than those formed near the top but these two types of bubble formation can be distinguished by sound and oscilloscope pattern.

In retorting runs PSR-8 and PSR-9 described earlier, in which unusually high losses of metal vapor occurred, the unstable boiling condition was clearly indicated by the "bump" detecting devices. Use of these detectors combined with better control of power input to the furnace has eliminated unstable boiling in subsequent runs.

²³ H. J. Metz and R. F. Hyland, Oak Ridge National Laboratory, private communication, 1965.

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FIG. I-24. Lead-Shielded Vibration Pickup Housing for Retorting Furnace. (EBR-II Fuel Reprocessing)

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FIG. I-25. Contact Microphone on Base Plate of Retorting Furnace.

D. FUEL CYCLE FACILITY OPERATIONS (C. E. STEVENSON, M. J. FELDMAN, D. C. HAMPSON)²⁴

Productive operations of the Fuel Cycle Facility (FCF) have been emphasized and accelerated during the past six months, consistent with the responsibility of the Facility for maintaining a fuel supply for the EBR-II reactor adequate to support its mission as a fast flux irradiation facility. A total of 65 irradiated fuel subassemblies discharged from the reactor was dismantled and the fuel was introduced to the process. No defective fuel elements were observed. Correspondingly, fabrication of 65 subassemblies from reprocessed fuel supplemented by unirradiated fuel pin castings prepared by the Metallurgy Division, Argonne, Illinois, was completed. Production of a modified fuel pin

²⁴ Idaho Division.

(Mark IA) expected to be capable of increased burnup was initiated. The new pin is slightly shorter and more highly enriched; modification of the shear station was required for its production. Examination and processing of the first reirradiated fuel in a subassembly (C-162) fabricated from irradiated fuel was conducted. Operation of the fuel element decanner-chopper machine was improved by separating the decanning and chopping functions. Arrangements were made to have the oxidized residue from melt refining processed at the Idaho Chemical Processing Plant (ICPP). An improved sodium-bond testing machine was devised and placed into service. Methods were

uevised and applied for the maintenance and repair of sealed master-slave manipulators. The plutonium

content of irradiated fuel and blanket material was determined.

1. Summary of Process Operations in the Fuel Cycle Facility (M. J. FELDMAN, D. C. HAMPSON)²⁴

Process operations were carried out effectively at Facility capacity with the manpower available. Considerable time was required for necessary maintenance and repair of equipment. The operations are summarized in Table I-8, and include processing of Mark IA fuel pins cast by the Metallurgy Division, Argonne, Illinois.

TABLE I-8. SUMMARY OF FUEL CYCLE FACILITY PROCESS OPERATIONS
(November 1965 through April 1966)

Operation	No. of Units	Operation	No. of Units
Irradiated subassemblies cleaned of sodium and dismantled	65	Injection casting operations	59
Fuel elements decanned, including process rejects	5863	Injection castings produced	6227
Melt refining ingots produced from discharged reactor fuel	37	Acceptable cast pins produced	5209
Total melt refining ingots produced, including recycled material	61	Fuel elements assembled and welded	6493 ^a
		Fuel elements passing leak test	6663 ^a
		Fuel elements bonded passing bond test	5777 ^a
		Subassemblies fabricated	65

^a Including 1937 fuel elements assembled from Mark IA pins fabricated at Argonne, Illinois (less than 1937 fuel elements in subsequent steps; see Section 2).

2. Fuel Modification and Associated Process Changes (V. G. ESCHEN)²⁴

a. FUEL ELEMENT DESIGN CHANGES TO INCREASE BURNUP POTENTIAL

The initial core fuel elements for the EBR-II reactor are presently limited to a burnup of 1.2% of the heavy atoms present (ANL-7125, p. 58) because of the limited void space available in the element for fuel pin expansion. Since the void space is partially occupied by sodium and since the fuel pin expands upon irradiation, the void space at reactor operating temperatures may become very small; and, if the stainless steel fuel cladding does not yield, the internal pressure of the compressed residual gas may approach failure stresses in the cladding. Consequently, a modified fuel element (designated as Mark IA), which provides greater void space, is being fabricated to increase fuel burnup potential. The length of the modified fuel pin has been shortened from 14.22 in. to 13.50 in. while the same fuel pin and cladding diameters, and the same overall cladding length have been retained. The length of the restraining plug at the upper end of the fuel element has correspondingly been increased from

2.73 in. to 3.45 in. To compensate for the reduced amount of uranium in the shorter pin, the nominal enrichment was increased from 48.1 to 52.2 a/o ²³⁵U.

b. PROCESS CHANGES REQUIRED

The reduction in fuel pin length affects only the operation of the pin processing and decanning machines and requires the provision of a longer restrainer; other process steps are unaffected. Since a large supply of Vycor²⁵ glass fuel element molds was available for production of elements of the original length, and use of shorter molds would require a change in the palette stand height, it was determined that it would be advantageous to retain the original casting length and simply shear a slightly greater amount from it. This increased somewhat the amount of metal recycled per casting. However, it was believed that this increase would be compensated by a reduced casting rejection rate by virtue of improved ability to shear potentially defective portions of the casting. Consequently, the

²⁵ Trademark of the Corning Glass Works for 96% Silica Glass.

injection casting operation was not affected by a change in the fuel length.

To produce the shorter length pin, the principal modification needed for the pin processing machine was alteration of the shear station. Adjustments were also required in the weighing balance (to provide for weighing an element of about 65 g instead of 68 g), in the length measuring station (extending the anvil to make up for the length difference), and in the data processor (to correct the calculation of fuel volume and to insert new value ranges). Rather than modify the existing three shear stations, it was decided to build new ones, since modification of the existing stations would require considerable machining, grinding, and welding on contaminated equipment. In addition, this afforded an opportunity to attempt the correction of minor difficulties encountered in the operation and maintenance of the existing shear station. The method of holding the fuel pin while shearing was improved by restricting bending of the pin; the shear blade holder was strengthened and the procedure for replacing the holder was simplified. The flow of shards into the shard receiver was also improved to avoid retention of shards in the station. A new shear station was installed, and its initial operation in the production of Mark IA fuel was very satisfactory; the acceptance rate in pin processing increased from a value of 71% for the preceding 16 runs on Mark I fuel to an average of 86% for the next 50 runs on Mark IA fuel. The increased acceptance rate was attributed to three factors: (1) The production of a better "cut" by the improved shear, as evidenced by a reduced rate of rejection because of shearing short of the required length, (2) since more defects occur near the ends of the casting, the probability of their removal was increased when the amount of fuel removed by the shear was increased (i.e., for a typical 16-in. casting, 1¾ in. is sheared off to make a Mark I element, and 2½ in. for a Mark IA fuel), and (3) the ability to position the casting with greater accuracy, thus increasing the certainty of choosing the area to be sheared.

With the modified shear, the life of the shear blades

also appears to have been extended to a level of about 1300 to 2000 elements sheared before failure, as compared with 1000 or less before failure of the previous shear. Other changes in the pin processing operation for use with Mark IA elements (weight and length measurements) have been carried out satisfactorily.

The decanner required only a slight change in its operation to make it suitable for use with the shorter Mark IA fuel element; no other equipment change was needed. The operational change involved a readjustment of the timing of the can cutting operation so that the cutting is interrupted slightly sooner, which occurs when the gap between the longer restrainer and the fuel pin is reached.

c. SUPPLEMENTARY MARK IA FUEL PIN PRODUCTION

Since the ability of the FCF to produce Mark IA fuel pins was limited by the time required to design and build a new shear station, an auxiliary supply of over two thousand Mark IA fuel pins was provided by fabrication of unirradiated fuel alloy in Argonne, Illinois. This enabled the placing of the Mark IA fuel under irradiation much sooner than would have been possible otherwise. Ingots of the proper enrichment were cast by the Chemical Engineering Division (ANL-7125, pp. 42-43), and these were then injection cast and processed to acceptable castings by the Metallurgy Division. Since it was necessary to conduct the latter operation in plutonium-contaminated gloveboxes, it was felt to be desirable to carry out all succeeding FCF operations in the Air Cell and Argon Cell to avoid plutonium contamination of the FCF sodium handling equipment and resultant increase in repair problems. Most of the production lot was also processed through FCF pin processing equipment to confirm element volume and to provide data for calculating the amount of sodium to be charged. The pins were then loaded into sodium-charged cans, welded, leak tested, bonded, bond tested, and placed into subassemblies using in-cell equipment according to standard operating procedures.

3. Examination of the First Reirradiated Fuel (J. P. BACCA, D. E. MAHAGIN, D. L. MITCHELL)²⁴

Irradiation of the first subassembly (C-162) which was fabricated from reprocessed irradiated fuel was completed, and the subassembly was transferred to the FCF for examination and processing. The fuel used in subassembly C-162 had been fabricated from reprocessed material (ingots from melt refining runs 1 and 2) obtained from subassemblies C-115, C-140,

B-304, and L-406, which had been irradiated to maximum burnups of 0.12 to 0.26 a/o, plus about 10% additional unirradiated fuel alloy, so that the average burnup value of the fuel used in the subassembly was equivalent to about 0.1 a/o. Subassembly C-162 was then reirradiated to a maximum additional burnup of 1.0 a/o.

TABLE I-9. COMPARISON OF IRRADIATION EFFECTS ON FUEL ELEMENTS MADE EITHER FROM IRRADIATED OR UNIRRADIATED ALLOY

Subassembly No.	Fuel Used in Fabrication	Reactor Row in Which Irradiated	Calculated Burnup (a/o)		Average Increase in Na Level (cm)	Average Void Volume (cc)	Average Internal Gas Pressure (atm)	Fuel Swelling (%) Calculated from	
			Max.	Avg.				Na level	Void volume
Pre-Irrad.	—	—	0	0	—	0.49	1.0	0	0
C-162	Irradiated ^a	2	0.99	0.84	1.5	0.34	1.16	3.6	4.2
C-138	Unirradiated	1	0.95	0.86	1.6	0.30	1.48	3.7	4.8
C-107	Unirradiated	5	1.03	0.78	1.6	0.32	1.25	3.8	4.4
B-306	Unirradiated	6	0.96	0.68	1.5	—	—	3.5	—
S-602	Unirradiated	3	1.01	0.84	1.6	0.34	1.11	3.8	3.9

^a Fuel fabricated from reprocessed material which had been irradiated to maximum burnups of 0.12 to 0.26 a/o plus about 10% additional unirradiated fuel alloy.

The exterior surface of the fuel elements appeared to be in normal condition after irradiation; no swelling of the cladding was indicated in a sample of 21 elements. The sodium level and bond quality were determined on a group of 45 elements. The average sodium level, at cell temperature, was 3.2 cm above the end of the fuel pin (the range was from 2.5 to 3.7 cm); bond quality was normal. The void volume and gas pressure were determined on a group of 44 elements. The average void volume was 0.34 cc, and the internal pressure was 1.16 atm at cell temperature. From these

data the swelling of the fuel was calculated to be 3.6% when based on the sodium level and 4.2% when based on the void volume. Measurements of declad fuel revealed no significant increase in pin diameter.

A comparison of these data with data for four subassemblies of similar maximum burnup (0.95 to 1.03 a/o) fabricated from unirradiated fuel is given in Table I-9. The similarity of the data indicates that up to this level of burnup the fuel growth is similar for fuel elements made either from unirradiated fuel or irradiated and refabricated fuel.

4. Equipment Maintenance and Modification

a. FUEL ELEMENT DECANNER MODIFICATION (D. L. MITCHELL,²⁴ J. WHITE²⁶)

Decanning of the fuel elements is accomplished by shearing off the ends of the can beyond the fuel section, removing the spiral wire wrap, and propelling the open-ended tube by means of skewed knurled-drive rolls against a lathe tool bit which then parts the can in the form of a narrow metal strip and peels it from the fuel pin. The original equipment also provided for simultaneously breaking the fuel pin into short pieces by passing the pin directly into a reciprocating slotted chopper bar, close to the decanner, which broke the pin into short pieces.²⁷ In operation, the chopping action was carried back by the moving fuel pin into the decanning portion of the machine, with adverse results. High speed photography of the operation of a spare decanner and chopper unit set up in an inert atmosphere glovebox showed that the forward progress of the fuel pin was momentarily halted during each chopping operation (approximately 10 times per fuel pin

decanned). The action of the chopper appeared to be exerted in two areas of the decanner. First, the driving rolls of the decanner continued to extrude the pin while its forward motion was restrained at the chopper. This resulted in bowing of the pin and placed a sidewise component of force on the drive roll bearings. Second, bowing of the pin changed its position relative to the stationary decanner tool, and increased the probability of chipping of the tool bit.

To overcome this problem, the decanning and chopping operations were separated into two steps. (The modification was designed by the Remote Control Division, Argonne, Illinois and its incorporation on the unit in the Argon Cell was carried out by the Idaho Division.) After the fuel element is decanned, the fuel pin is driven by the decanner drive rolls into an open ended, heated, horizontal tube (heating is needed to prevent the sodium-coated pin from adhering to the tube). The tube is then rotated to a vertical position, and the pin drops by gravity into a reciprocating chopping bar. The chopped pieces drop as usual through a funnel into a charging tray. The two-step operation requires slightly more time (about 30 seconds) per

²⁶ Remote Control Division, Argonne, Illinois.

²⁷ ANL-6106, pp. 17-20.

element, but operating with this procedure has shown that time lost for repairs is greatly decreased.

The bearings used on the decanner drive rolls initially consisted of silver-impregnated graphite sleeves; this type of bearing wore erratically and on many occasions failed rapidly. The sleeve bearings have been replaced by needle bearings which are lubricated with a radiation resistant oil (NRRO-360). With unhardened shafts, the first set of needle bearings operated satisfactorily for the decanning of several thousand elements; this may be compared with lifetimes of the order of 500 elements observed for graphite sleeve bearings. Hardened shafts have since been installed, and the needle bearings are expected to show even greater lifetimes.

b. IMPROVED BOND TESTER (J. P. BACCA)²⁴

Refabricated fuel elements after the impact-bonding step (ANL-7055, pp. 76-77) are examined in the Air Cell for discontinuities in the sodium bond and the height of the sodium above the upper end of the clad fuel pin. The technique employed, which depends upon passing the element through an eddy-current coil, is described in ANL-6724. Operation of the detection machine was generally most satisfactory. However, as previously reported (ANL-7055, p. 77), after about 10,000 test operations, wear was noted at a number of points on various components and the maintenance time required became somewhat excessive. The original machine which was used for at least another 6000 test operations has been replaced by a new machine of improved design (Figure I-26). The principle of bond testing has not been changed.

The major modifications incorporated in the design of the new bond-testing machine are the following: (1) a collet is used to grip the fuel element for locating it in the eddy-current coil in place of the spring fingers used previously, as the fingers required frequent repair, (2) the collet drive motor is remotely replaceable, (3) the eddy-current coil was made remotely replaceable, (4) the heaters were made remotely replaceable and are zoned to produce a more uniform heated zone. In addition, most of the remaining components have been redesigned to increase their working lifetime and to improve the ease of remote maintenance or replacement. After some adjustments and minor modifications, operation of the new equipment was satisfactory. It is planned to construct a duplicate machine for use as a spare; meanwhile the original machine will serve for this purpose.

c. MASTER-SLAVE MANIPULATOR MAINTENANCE (D. M. PAIGE, J. O. KLEFFNER)²⁴

Six Model A master-slave manipulators are installed in the shielding wall of the Argon Cell to assist in

carrying out the following process operations: decanning, charging and discharging the injection casting furnace, pin processing, fuel element assembly and welding, and miscellaneous equipment repair. The Model A manipulator incorporates individually removable master and slave ends. Movement of the master end is transmitted to the slave end via a rotating shaft in a through-the-wall sleeve containing rotary seals to preserve the integrity of the inert atmosphere within the cell. Operation of these manipulators during the past two years has been relatively satisfactory. Repair of the master ends is straightforward, since they can be removed without interfering with operation of the cell. The slave ends can also be removed; however, their repair is more difficult because of the degree of contamination characteristic of all Argon Cell equipment.

Initially, it was planned to employ a glovebox system for carrying out repairs of the Model A slave ends. This system consisted of a portable glovebox into which the slave end could be lowered through the floor hatch in the Air Cell, and a fixed glovebox (which was connected to the building exhaust system) into which the slave end could be transferred for repair. However, as the level of equipment contamination increased, the glovebox system became impractical for the following reasons:

(1) The radiation level from the slave ends was sufficiently high (several R/hr at 1 ft) to restrict the working time in the gloveboxes. Even after the exposed portions of the slave ends were wiped off, the working time for an individual was limited to about 1 hour per month. This factor influenced the overall repair problem in two ways. First, overall manpower requirements were high; for example, the replacement of the tapes in one slave end required 15 man-months of radiation exposure. Second, the limited working time causes persons to hurry and thereby increases the possibility for mistakes.

(2) Repair of specific malfunctions resulted in returning slave ends to the cell with other components that were worn but had not yet failed. These components, then, were subject to early failure.

Based on these considerations, it was decided that a periodic major overhaul of the slave ends would be more economical than waiting to carry out specific repairs on them. Accordingly, when a slave end was removed from the cell, it was decontaminated (with detergent solutions) and overhauled. This included replacement of all gears, tapes, bearings, and other items that are subject to deleterious wear.

Complete overhaul of all nine slave ends has been accomplished and they have been returned to service. There were no restrictions on personnel working time

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FIG. I-26. Improved Bond Tester.

since the slave ends were adequately decontaminated. However, since the surfaces were still slightly contaminated, the repair work was performed using gloves and other protective clothing in a plastic-walled room with adequate ventilation. The cost of repairing each end was estimated to be less than one-third the cost of purchasing a new slave end.

Repairs have also been made of the gear units on the in-cell side (or slave end) of the through-the-wall sleeves. The repairs were done in the following manner.

The master end was first removed, and a long, narrow glovebox containing an argon atmosphere was then attached to the outer flange of the sleeve. After the seal ring was loosened, the sleeve was then drawn into the glovebox; as the sleeve was being withdrawn it pulled a plug behind it to preserve the cell atmosphere. Gear units on the end of the sleeve were then changed by working through gloved ports without excessive radiation exposure to the hands. The sleeve was then pushed back into place and the seal ring was tightened.

5. Skull Oxide Disposition and Treatment (N. SWANSON, R. M. FRYER)²⁴

In the melt refining operation, in which volatile and chemically active fission products are removed from the fuel alloy, a residue or skull containing about 5% of the alloy charged remains in the crucible when the ingot is poured. It was initially intended that the uranium in the skull be recovered at least on a demonstration basis, by the EBR-II Skull Reclamation Process (ANL-6818; this report, Section IC). The development of this process is substantially completed. In the process, the skull is removed from the crucible by reacting it with an oxygen-argon mixture at about 800°C (ANL-6874; ANL-6900, pp. 116-123); a free-flowing powder is formed (the uranium is converted to U_3O_8). The skull oxide (typically weighing 0.5 to 1.0 kg) is then transferred to a zinc can (5.4-in. dia. by 6-in. high) using the dumping device described in ANL-6800, pp. 168-175. The zinc can was used because of its compatibility in the process. The can, along with the oxide, will be charged to the reduction furnace.

At present, a considerable number of zinc cans containing skull oxide are in storage in the Argon Cell. Since the installation of equipment for the skull reclamation process has been postponed, it was necessary to

consider other means of handling the skull oxide. Arrangements have been made with the Idaho Chemical Processing Plant (ICPP), National Reactor Testing Station, Idaho, for storage and for processing of the skull oxide for recovery of the uranium. The processing method which ICPP plans to use involves leaching the U_3O_8 from the skull oxide with HNO_3 .

Since it is possible that pieces of the zirconia crucible used in melt refining may be included with the skull oxide as a result of crucible breakage during or after the oxidation step, it was believed necessary that the leaching be done in a dissolver containing a small, removable basket to permit removal of the crucible pieces and avoid their accumulation in process vessels. The only equipment available at the ICPP for this purpose has a removable basket which is too small to accommodate the zinc can. Consequently, a device (Figure I-27) was constructed for transferring the skull oxide from the zinc can to a tall, small diameter aluminum can (3½-in. dia. by 13 in. high) which would be compatible with the ICPP processing equip-

FIG. I-27. Equipment for Transfer of Skull Oxide to Aluminum Cans.

...ent; the aluminum can is dissolved in the nitric acid leaching process. The transfer device consists of a portable dumper housing equipped with a blower and absolute filter (to minimize cell atmosphere contamination with radioactive dust). As shown in Figure I-27, with the dumper housing displaced, the housing encloses an externally operated tipping device (dumper),

a funnel, and a holder for the aluminum can. The can holds about 2 kg of skull oxide which enables the compositing of batches of oxide to reduce storage and handling requirements. The transfer device has been operated satisfactorily to load more than 20 aluminum cans, most of which have been shipped to the ICPP.

6. Analyses of Irradiated Fuel Subassembly and Blanket Rods (E. R. EBERSOLE, M. T. LAUG, W. R. SOVEREIGN)²⁴

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FIG. I-28. Maximum Plutonium-239 Content and Burnup Versus Increase in Uranium-236 for Row 2 Subassemblies from EBR-II Reactor.

a. CORRELATION OF FUEL SUBASSEMBLY BURNUP DATA

Relative axial and radial burnup values have been determined for irradiated fuel pins from thirteen subassemblies located in Rows 1 through 6 of the EBR-II reactor by a method that involves the direct counting of the 0.72 to 0.77 Mev gamma of ^{95}Zr - ^{95}Nb through a collimated aperture in the 5-ft thick wall of the Air Cell (ANL-6900, pp. 77-78). The subassemblies were removed at various fuel burnup increments which ranged from 0.1 to 1.0 a/o. Segments cut from selected gamma-counted pins were then analyzed for absolute burnup by the determination of the stable fission product lanthanum-139 using a mass spectrometric isotope dilution technique (ANL-6900, p. 338). Relative axial and radial burnup values were converted to absolute values by multiplying the measured zirconium-niobium activity by the ratio of absolute burnup to zirconium-niobium activity for the selected pin segments. Because of an uncertainty in the lanthanum-139 fission yield, a $\pm 10\%$ uncertainty must be assigned

to the absolute burnup data, although the precision of the method is estimated to be $\pm 2\%$. The measured values have been compared with calculated values furnished by the EBR-II Reactor Physics Group, Idaho. The agreement between the two sets of values is reasonably good; the measured values showed an average deviation of $+1.8\%$ from the theoretical values for the thirteen subassemblies.

b. PLUTONIUM ANALYSES OF FUEL SUBASSEMBLIES

The production of both ^{239}Pu and of ^{236}U in an irradiated fuel (core) subassembly is a function of the neutron flux and is consequently related to burnup. This relationship has been confirmed by analysis of a series of samples obtained from subassemblies irradiated in Row 2 of the EBR-II reactor as shown in Figure I-28. With these ratios established for the EBR-II reactor, both burnup and plutonium information may be deduced from data for the increase in ^{236}U content ($\Delta^{236}\text{U}$) if radial and axial variations are

FIG. I-29. Axial Variations in Ratios of Plutonium and of Burnup to Increase in Uranium-236.

TABLE I-10. RATIO OF PLUTONIUM-239 CONTENT TO BURNUP VALUES IN CORE SUBASSEMBLIES

Core Sub-assembly	Position in Core	Fuel Pin No.	Max. Burnup (a/o)	^{239}Pu ($\mu\text{g/g}$ Fuel)	Ratio $^{239}\text{Pu/a/o}$ Burnup
C-138	1A1	26	0.966	826	854
C-140	2A1	78	0.274	233	851
C-143	2C1	21	0.446	379	850
C-122	2F1	3	0.618	525	850
C-103	2D1	3	0.744	635	854
C-112	4F2	87	0.411	352	855
C-131	5D2	21	0.588	506	860
B-304	6C4	5	0.169	160	946

TABLE I-11. PLUTONIUM CONTENT AND BURNUP VALUES OF AXIAL BLANKET RODS

From Fuel Subassembly		Max. Burnup in Fuel Sub-assembly (a/o)	Axial Blanket Rod Sample		
No.	EBR-II position		Location	Total Pu content ($\mu\text{g/g}$ U)	Burnup (a/o)
C-104	3E2	1.21	$\sim\frac{3}{8}$ in. from top end of lower blanket	1144	0.025
C-104	3E2	1.21	$\sim\frac{3}{8}$ in. from bottom end of lower blanket	138	0.0022
C-143	2C1	0.495	$\sim\frac{3}{8}$ in. from bottom end of upper blanket	440	0.0081
C-140	2A1	0.274	$\sim\frac{3}{8}$ in. from bottom end of upper blanket	204	0.0047

taken into account. Estimation of burnup and plutonium-239 production from $\Delta^{236}\text{U}$ data on fuel from the reactor will provide adequate data for reprocessing control along with a significant reduction in the analytical time.

Axial variation in the ratios of the ^{239}Pu to burnup and of the burnup to $\Delta^{236}\text{U}$ is given in Figure I-29. The change in these ratios reflects a change in the neutron energy spectrum along the axis of the reactor.

The ratios of ^{239}Pu to burnup for fuel pins from four Row 2 subassemblies and from four radially oriented subassemblies at different burnup levels are given in Table I-10. The ratios are remarkably constant and ranged from 850 to 860 $\mu\text{g Pu/(g)}$ (a/o burnup), until the edge of the core was approached, where a value of 946 $\mu\text{g Pu/(g)}$ (a/o burnup) was obtained for a Row 6 subassembly. This change probably reflects a change in the neutron spectrum in this region.

c. PLUTONIUM AND BURNUP ANALYSES OF AXIAL BLANKET RODS

Some information has also been obtained on the plutonium content and burnup values of axial blanket rods at core fuel burnup values of up to 1.2 a/o. These data, based on analyses of samples obtained from blanket rods, are summarized in Table I-11. A maximum plutonium content of about 0.11 w/o and a maximum burnup value of 0.025 a/o were found in a sample obtained near the upper end of the lower blanket. The precision of the measurement of the plutonium content is estimated to be $\pm 2\%$, and that of the blanket burnup to be $\pm 10\%$.

II

Fluidization and Volatility Processes¹

(A. A. Jonke, J. J. Barghusen)

INTRODUCTION

The objective of the fluoride volatility program is to develop the technical data required for the design of an all-volatility commercial plant for the reprocessing of power reactor fuels. Currently, major attention is being directed toward the demonstration of fluoride volatility processes for low-enrichment $\text{UO}_2\text{-PuO}_2$ fuel clad in Zircaloy. Two alternative process flowsheets, described in ANL-7055, pp. 99-102, are being considered for this type of fuel. In one concept, the fuel is contacted directly with oxygen and fluorine to form UF_6 and PuF_6 which are subsequently separated from each other. The other flowsheet, the interhalogen process, is based on the use of bromine pentafluoride to convert uranium to volatile UF_6 while plutonium remains as nonvolatile plutonium tetrafluoride. Plutonium is recovered as volatile PuF_6 in a subsequent step by reaction with fluorine.

Laboratory-scale experiments are being performed to define the optimum conditions for carrying out the fluorination steps in both processes using $\text{UO}_2\text{-PuO}_2$ pellets containing simulated fission product oxides. The major steps in the process based on the direct fluorination of the oxide fuel with a mixture of oxygen and fluorine are being demonstrated with $\text{UO}_2\text{-PuO}_2$ fuel in an engineering-scale alpha facility. Engineering devel-

opment work on the interhalogen flowsheet is also under way.

In connection with the potential application of fluid-bed fluoride volatility processes to the reprocessing of fast breeder reactor fuels, an economic evaluation has been made² of volatility processing of the core and blanket of hypothetical fast breeder reactors that might be in commercial operation in 1980. In this evaluation, conceptual processing plant designs were made and costs estimated for processing of oxide, carbide, and metal fuels from reactors of a nominal 1000 Mw(e) size. The evaluation involved a cost comparison of volatility with aqueous and pyrochemical plants for processing, waste disposal, and out-of-reactor inventory. Significant cost advantages were shown for volatility processing relative to aqueous processing for all fuels and for all plant sizes. The cost advantages of volatility to aqueous processing were derived primarily from the relatively few and small size of process equipment items for volatility processing, from the short cooling time required for the discharged fuel before processing and from the concentrated, solid form of the high-level activity product wastes generated in the volatility process.

² M. Levenson, V. G. Trice, Jr., and W. J. Mecham, Comparative Cost Study of the Processing of Oxide, Carbide, and Metal Fast Breeder Reactor Fuels by Aqueous, Volatility, and Pyrochemical Methods, ANL-7137, May 1966.

¹ A summary of this section is given on pages 6 to 11.

A. LABORATORY INVESTIGATIONS (M. J. STEINDLER)

1. Fluorination of UO_2 - PuO_2 -Fission Product Pellets in a 2-inch Diameter Fluidized-Bed Reactor (L. J. ANASTASIA, P. G. ALFREDSON,³ G. W. REDDING, M. HAAS)

Studies are being carried out in a 2-in. dia. fluid-bed reactor to define conditions for the fluorination of UO_2 - PuO_2 -fission product (F.P.) pellets that would ensure a minimum retention of uranium and plutonium on the alumina particles of the fluidized bed.

Two fluorinating agents are being evaluated for the processing of UO_2 - PuO_2 -fission product pellets: fluorine and bromine pentafluoride (BrF_5). One method for fluorination with fluorine utilizes a simultaneous oxidation-fluorination method⁴ whereby the fuel pellets are oxidized with oxygen in the lower zone of the fluid-bed reactor and the fines resulting from the oxidation are fluorinated with fluorine to volatile hexafluorides in the upper zone of the reactor. More than 99% of the uranium and about 75% of the plutonium are removed from the alumina bed as volatile hexafluorides during two-zone oxidation-fluorination at 450°C. Further removal of plutonium and uranium is accomplished by recycle-fluorination with 90 v/o fluorine at temperatures up to 550°C. A modified process (a two-step process) is also being evaluated. In this process, the fuel is oxidized to U_3O_8 - PuO_2 fines and then fluorinated with fluorine in separate steps. By the use of this processing sequence, it is possible to initiate the fluorination step at lower temperatures (300 to 350°C) than in the two-zone concept. Apparently, by initiating the fluorination step at low temperatures, it is possible to achieve somewhat higher plutonium removal from the alumina bed material.

In the alternative process, bromine pentafluoride is used as a selective fluorinating agent for separation of uranium as UF_6 from uranium-plutonium mixtures. Since sintered oxide fuel does not react readily with BrF_5 , the oxide fuel is oxidized to U_3O_8 - PuO_2 powder prior to fluorination. Only uranium is volatilized as the hexafluoride product during fluorination with BrF_5 ; the plutonium, which remains as solid PuF_4 in the fluid bed, is recovered as PuF_6 in a subsequent step by recycle-fluorination with fluorine.

Two types of UO_2 - PuO_2 -F.P. pellets have been used in these studies: Type I pellets were fabricated from solid-solution UO_2 - PuO_2 mixed with fission product

oxides and sintered to 94% theoretical density in 6 v/o hydrogen-nitrogen at 1600°C for 2 hr; Type II pellets were fabricated from a powdered mixture of UO_2 , PuO_2 , and fission product oxides and were sintered to about 88% theoretical density in 6 v/o hydrogen-nitrogen at 1700°C for 6 to 8 hr. Since cesium is not present in the pellets, cesium fluoride has been added to the alumina beds to simulate more closely the fission product distribution which would exist in the re-processing of irradiated fuels.

In previous experiments (ANL-7125, pp. 62-66), increased plutonium retention was observed in runs with Type II pellets and in which cesium fluoride was added to the alumina bed, as compared with plutonium retention in runs in which Type I pellets were used in the absence of cesium fluoride. Several experiments have been completed to separate the effects of cesium fluoride and the use of fuel pellets with different characteristics on plutonium retention in the alumina bed. Also, the effects on plutonium retention in the alumina bed of the pellet charge-to-alumina charge ratio and the manner in which the increase in reaction temperature was programmed during recycle-fluorination were determined for the two-zone oxidation-fluorination process. In addition, the results from two runs using the stepwise oxidation and fluorination procedure with fluorine are reported. The results of seven experiments with BrF_5 as the fluorinating agent are described. In these runs, the BrF_5 step was carried out at a temperature of 200, 300, or 400°C, and various recycle-fluorination sequences with elemental fluorine at temperatures from 200 to 600°C were evaluated with respect to plutonium removal.

a. EQUIPMENT AND PROCEDURES

The major components in the experimental system are the 2-in. dia. fluidized-bed reactor, a hexafluoride collection system, a thermal conductivity cell for continuous fluorine analysis, a fluorine disposal system, and a remote-head diaphragm pump. These components, which are contained in an alpha glovebox, have been described previously (ANL-6925, p. 116). A detailed description of the experimental procedure has also been reported (ANL-7055, p. 110). The BrF_5 -disposal system consists of three primary soda lime traps in parallel and one secondary soda lime trap, each 4 in. in dia. by 24 in. high. During the BrF_5 fluorination

³ Guest Scientist from the Australian Atomic Energy Commission.

⁴ L. J. Anastasia and W. J. Mechem, Oxidation-Fluorination of Uranium Dioxide Pellets in a Fluidized Bed, Ind. Eng. Chem., Process Design Develop. 4(3), 338-344 (July 1965).

step, UF_6 , bromine, and unreacted BrF_5 are removed from the reactor effluent gas by reaction with soda lime at about 100°C in the primary traps. At all times a single primary trap and the secondary trap are used in series for disposal purposes.

In the runs reported below, 650 g of $\text{UO}_2\text{-PuO}_2$ -fission product pellets, corresponding to a 2-in. deep pellet bed, and 1100 g of nominal 48 to 100 mesh sintered alumina, corresponding to a static depth of 12 in., were generally used. In most runs, 0.6 g CsF was also added to the alumina bed. The pellets contained approximately 0.4 w/o plutonium as PuO_2 , 86 w/o uranium as UO_2 and 1 w/o fission products as the oxides. In Table II-1 are given the concentrations of fission products as oxides in Type II fuel pellets, determined by analysis; the composition of Type I pellets was reported in ANL-7055, p. 111.

b. FLUORINATION OF $\text{UO}_2\text{-PuO}_2\text{-F.P. PELLETS}$ WITH FLUORINE

(1) Two-Zone Oxidation-Fluorination

(a) EFFECT OF CESIUM FLUORIDE ADDITION AND THE USE OF TYPE II PELLETS

Three runs were made with Type II pellets and no cesium fluoride added to the alumina bed (Table II-1). It was desired to determine the effect on uranium and plutonium retention in the alumina of (1) added cesium fluoride and (2) using Type II pellets rather than Type I pellets; also of interest was the reproducibility of the experimental data. The reaction conditions (Table II-2) for the three runs with Type II pellets and no added cesium fluoride (runs Pure-10, -12, and -14) were similar to the conditions for an earlier run (Pure-6, ANL-7125, p. 63) with Type I pellets and no added cesium fluoride and for another previous run (Pure-8, ANL-7125, p. 63) with Type II pellets and cesium fluoride added. The results of these runs are compared in Table II-3. For the process involving two-zone oxidation-fluorination followed by a recycle-fluorination sequence of 1 hr at 450°C , 3 hr at 500°C , and 8 hr at 550°C , the differences between Types I and II pellets apparently do not have a significant effect on plutonium retention in the alumina bed, but the addition of cesium fluoride leads to increased retention of both uranium and plutonium. The results of the replicate experiments indicate that adequate reproducibility can be achieved in these types of tests. The effect of the added cesium can be minimized by using a two-step separate oxidation-fluorination process as described below.

TABLE II-1. COMPOSITION OF $\text{UO}_2\text{-PuO}_2\text{-FISSION}$ PRODUCT TYPE II PELLETS

Oxide	Concentration in Pellets (w/o)	
PuO_2	0.48	
UO_2	98	
BaO	0.010	This group of fission product oxides has been used in previous work on the fluid-bed fluorination of $\text{U}_3\text{O}_8\text{-PuO}_2\text{-F.P.}$ oxide mixtures in a 1.5-in. dia. reactor. ^a
Ce_2O_3	0.079	
Eu_2O_3	0.0006	
Gd_2O_3	<0.0004	
La_2O_3	0.027	
Nd_2O_3	0.19	
Pr_6O_{11}	0.058	
Sm_2O_3	0.033	
Y_2O_3	0.015	
ZrO_2	0.18	
MoO_3	0.094	
Ag_2O	<0.0005	
CdO	<0.002	
In_2O_3	0.0005	
Nb_2O_5	<0.0004	
PdO	—	
RhO_2	0.026	
RuO_2	0.063	
SrO	0.033	

^a R. L. Jarry, A. V. Hariharan, J. Fischer, M. J. Steindler, J. J. Stockbar, T. D. Baker, W. H. Gunther, and G. W. Redding, Laboratory Investigations in Support of Fluid-bed Fluoride Volatility Processes. Part IX. The Fluid-bed Fluorination of Plutonium-containing Simulated Oxidic Nuclear Fuel in a $1\frac{1}{2}$ -inch-diameter Reactor, ANL-7077, December 1965.

(b) EFFECT OF PELLET-TO-ALUMINA CHARGE RATIO

A series of three runs was made to determine the effect of the pellet-to-alumina charge ratio on plutonium volatilization from the alumina bed. In these runs, $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellet charges of 0.33 (run Pure-11), 0.65 (run Pure-8), and 1.32 kg (run Pure-13) were used with 1100 g of alumina to give the corresponding pellet charge-to-alumina charge ratios of 0.3, 0.6, and 1.2, respectively. The corresponding pellet bed depths were 1, 2, and 4 in. In each run, cesium fluoride was added to the alumina bed in proportion to the pellet charge (~ 1 g CsF /kg pellets). The pellets were reacted in a sequence of two-zone oxidation-fluorination and single-zone fluorination at 450°C , followed by recycle-fluorination for 1 hr at 450°C , 3 hr at 500°C , and 8 hr at 550°C . Operating conditions for runs Pure-11 and Pure-13 for the 1- and 4-in. pellet beds are given in Table II-2; the experiment with a 2-in. bed of pellets,

TABLE II-2. AVERAGE OPERATING CONDITIONS—RUNS PURE-10 TO PURE-16

Equipment: 2-in. dia. fluid-bed reactor

UO₂-PuO₂-F.P. pellets (Type II): 0.5-in. dia. by 0.4-in. right cylinders

Alumina bed: Alcoa T-61 alumina, nominal 48 to 100 mesh (−170 mesh fraction removed)

Bed support: Nickel balls

Diluent gas: Nitrogen

	Pure-10	Pure-11	Pure-12	Pure-13	Pure-14	Pure-15	Pure-16
<i>Material Charged to Reactor</i>							
Weight of UO ₂ -PuO ₂ -F.P. pellets (g)	635.7	332.9	651.6	1317.2	654.3	718.1	661.1
Pellet bed depth (in.)	2	1	2	4	2	2	2
Weight of alumina (g)	1100	1100	1100	1100	1100	1200	1100
Alumina bed depth (in.)	12	12	12	12	12	13	12
Weight of cesium fluoride (g)	—	0.3	—	1.2	—	0.6	0.6
<i>Two-Zone Oxidation-Fluorination at 450°C</i>							
Cumulative process time (hr)	0-3.0	0-1.5	0-3.0	0-5.0	0-3.0	0-3.0	0-3.0
Reactor pressure (mm Hg)	1420	1400	1480	1480	1440	1480	1500
Superficial gas velocity ^a (ft/sec)	0.7	0.7	0.7	0.6	0.7	0.7	0.7
Oxygen concentration to pellet bed (v/o)	20	20	21	0-20	20	21	21
Fluorine concentration to fluid bed (v/o)	10	10	8	8	10	10	8
<i>Single-Zone Fluorination at 450°C</i>							
Cumulative process time (hr)	3.0-4.0	1.5-2.0	3.0-4.0	5.0-6.0	3.0-4.0	—	—
Reactor pressure (mm Hg)	1370	1340	1340	1410	1240	—	—
Superficial gas velocity ^a (ft/sec)	0.7	0.6	0.7	0.7	0.7	—	—
Fluorine concentration to fluid bed (v/o)	12	12	10	10	10	—	—
<i>Recycle-Fluorination with 90 v/o Fluorine</i>							
Cumulative process time (hr)	4.0-17.0	2.0-14.0	4.0-16.0	6.0-18.0	4.0-16.0	3.0-11.0	3.0-11.0
Reactor pressure (mm Hg)	1370	1360	1360	1390	1330	1380	1360
Superficial gas velocity ^a (ft/sec)	0.8	0.8	0.8	0.8	0.4	0.3	0.7
Cumulative process time at 450°C (hr)	4.0-5.0	2.0-3.0	4.0-5.0	6.0-7.0	4.0-5.0	3.0-4.0	3.0-4.0
Cumulative process time at 500°C (hr)	5.0-9.0	3.0-6.0	5.0-8.0	7.0-10.0	5.0-8.0	4.0-7.0 ^b	4.0-10.0 ^b
Cumulative process time at 550°C (hr)	9.0-17.0	6.0-14.0	8.0-16.0	10.0-18.0	8.0-16.0	7.0-11.0	10.0-11.0

^a Based on the cross-sectional area of the reactor and calculated for operating temperature and pressure.^b Temperature was increased from 450 to 550°C during this period, at 5°C/9 min in run Pure-15 and 5°C/18 min in run Pure-16.

run Pure-8, was reported previously (ANL-7125, pp. 62-66).

The duration of the two-zone oxidation-fluorination and the single-zone fluorination steps was 2 hr with the 1-in. bed of pellets (Pure-11), 5 hr with the 2-in. bed (Pure-8), and 6 hr with the 4-in. bed (Pure-13). During these periods, 99% of the uranium and 60 to 70% of the plutonium was volatilized from the alumina bed. The course of removal of plutonium from the alumina bed during recycle-fluorination in these runs is shown in Figure II-1. The uranium and plutonium concentrations in the final alumina beds were 0.010 w/o (for both uranium and plutonium), 0.020 w/o U and 0.014 w/o Pu, and 0.030 w/o U and 0.024 w/o Pu for the 1-, 2-, and 4-in. deep pellet beds, respectively. These concentrations correspond to volatilization of greater than 99.9% of the uranium and 92.5, 94.7, and 95.3% of the plutonium for pellet-to-alumina weight ratios of 0.3, 0.6, and 1.2, respectively, in a single use of the alumina bed. Thus, the plutonium retention in the alumina bed did not increase proportionally with increases in the pellet charge and, consequently, the extent of vola-

TABLE II-3. EFFECT OF CESIUM FLUORIDE ADDITION AND TYPE OF FUEL PELLETS ON FINAL URANIUM AND PLUTONIUM CONCENTRATIONS IN ALUMINA BEDS

Charge:

UO₂-PuO₂-F.P. pellets: ~650 g

Alumina: 1100 g

Reaction Sequence:

Two-zone oxidation-fluorination: 3 hr

Single-zone fluorination: 1-2 hr

Recycle-fluorination: 450°C 1 hr
500°C 3-4 hr
550°C 8 hr

Run	Pellet Type	CsF Addition	Final Alumina Bed		
			U (w/o)	Pu (w/o)	
Pure-10	II	No	0.010	0.010	Replicate Experiments
Pure-12	II	No	0.006	0.006	
Pure-14	II	No	0.004	0.008	
Pure-6 ^a	I	No	0.004	0.007	
Pure-8 ^a	II	Yes	0.024	0.014	

^a These runs previously reported, ANL-7125, pp. 62-66.

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FIG. II-1. Effect of Initial Pellet Charge-to-Alumina Charge Ratio on Plutonium Retention in Alumina Fluidized Beds during Recycle-Fluorination Step.

Initial UO_2 - PuO_2 -F.P. Pellet Charge

Pure-11: 0.33 kg; 1-in. depth

Pure-8: 0.65 kg; 2-in. depth

Pure-13: 1.32 kg; 4-in. depth

tilization of plutonium from the alumina bed was improved by increasing the pellet charge-to-alumina charge ratio from 0.3 to 1.2.

(c) EFFECT OF PROGRAMMED TEMPERATURE INCREASE DURING RECYCLE-FLUORINATION

Two runs were made with fluorine as the fluorinating agent to determine whether a programmed temperature increase from 450 to 550°C over a given time period would be effective in reducing the plutonium concentration in the final alumina bed to a satisfactory level. In run Purse-4, with BrF_5 as the fluorinating agent (described in a following section), a final plutonium concentration in the bed of 0.006 w/o was achieved by use of a programmed temperature increase. This concept was investigated in runs Pure-15 and -16 during recycle-fluorination, following the two-zone oxidation-fluorination step, in an effort to reduce residual plutonium to low levels. Operating conditions for these runs are given in Table II-2. After one hour of recycle-fluorination at 450°C, the reactor temperature was raised to 550°C in increments of 5°C/9 min for 3 hr in run Pure-15, and in increments of 5°C/18 min for 6 hr in run Pure-16. In both runs, the total recycle-fluorination time of 8 hr was completed by subsequent recycle-fluorination at 550°C.

Uranium and plutonium concentrations in the final alumina bed in run Pure-16 were 0.016 w/o and 0.034 w/o, respectively, whereas in run Pure-15, with a more rapid increase in temperature from 450 to 550°C during recycle-fluorination, the concentrations of residual uranium and plutonium in the final alumina bed were 0.038 w/o and 0.025 w/o, respectively. In a previous run, Pure-7 (ANL-7125, pp. 62-65), wherein reactor temperature was raised from 450 to 550°C over 0.5 hr during recycle-fluorination, the final uranium and plutonium concentrations in the alumina bed were both 0.018 w/o.

The results from runs Pure-15 and -16 showed that a programmed increase in temperature from 450 to 550°C did not result in increased removal of plutonium from the bed material. Plutonium removal was less satisfactory than that obtained in run Pure-8 (see Table II-3—final uranium and plutonium concentrations of 0.024 and 0.014 w/o, respectively) which used a recycle-fluorination sequence of 1 hr at 450°C, 3 hr at 500°C and 8 hr at 550°C.

(2) Two-Step Oxidation-Fluorination Experiments

Comparison of the data from the Pure runs reported above with the results of initial runs with BrF_5 as the fluorinating agent (described below) indicated that one or both of the following conditions were necessary to achieve a low plutonium concentration on the alumina bed when cesium fluoride was present: (a) an initial low temperature of fluorination ($\sim 300^\circ\text{C}$), and (b) removal of $\sim 99\%$ of the uranium prior to volatilization of any plutonium. Runs Pure-17 and -18 were completed to study these effects using fluorine as the fluorinating agent. The runs were carried out in a two-step processing sequence of pellet oxidation, followed by fluorination with dilute fluorine (< 20 v/o fluorine) for removal of the bulk of the uranium, and then recycle-fluorination with 90 v/o fluorine; operating conditions are shown in Table II-4.

In run Pure-17, fluorination of the oxidized pellets was initially attempted at 300°C with 10 v/o fluorine; however, under these conditions, the uranium fluorinated slowly, as shown in Figure II-2. After 2.5 hr of operation at this temperature, only 20 to 30% of the uranium charge had been fluorinated. After this period, the temperature was raised to 350°C and maintained at this temperature for 3 hr. At 350°C the production rate of UF_6 was about a factor of 3 higher than at 300°C. In run Pure-18 (Figure II-3), a 2-hr fluorination period at 350°C with 16 v/o fluorine was sufficient to fluorinate most of the uranium to hexafluoride product, corresponding to an average production rate for this period of about 40 lb UF_6 /(hr)(sq ft).

TABLE II-4. AVERAGE OPERATING CONDITIONS—RUNS PURE-17 AND PURE-18

<i>Equipment:</i>	2-in. dia. fluid-bed reactor
<i>UO₂-PuO₂-F.P. Pellets (Type II):</i>	
Size:	0.5-in. dia. by 0.4-in. right cylinders
Weight:	~650 g
Bed depth:	2 in.
<i>Alumina Bed:</i>	
Material:	Alcoa T-61 alumina
Size limits:	nominal 48 to 100 mesh (−170 mesh fraction removed)
Weight:	1100 g
Static bed depth:	12 in.
<i>Weight of Cesium Fluoride:</i>	0.6 g
<i>Bed Support:</i>	Nickel balls
<i>Diluent Gas:</i>	Nitrogen

	Run Pure-17	Run Pure-18
<i>Oxidation at 450°C</i>		
Cumulative process time (hr)	0-4.0	0-4.0
Reactor pressure (mm Hg)	960	980
Superficial gas velocity ^a (ft/sec)	0.8	0.7
Oxygen concentration to pellet bed (v/o)	19	20
<i>Fluorination (Once-through Flow)</i>		
Cumulative process time (hr)	4.0-9.5	4.0-6.0
Reactor pressure (mm Hg)	1470	1500
Superficial gas velocity ^a (ft/sec)	0.6	0.6
Fluorine concentration to fluid bed (v/o)	10 ^b	16 ^c
Temperature (°C)	300°C, 4.0-6.5 hr 350°C, 6.5-9.5 hr	350
<i>Recycle-Fluorination with 90 v/o Fluorine</i>		
Cumulative process time (hr)	9.5-21.5	6.0-16.0
Reactor pressure (mm Hg)	1430	1380
Superficial gas velocity ^a (ft/sec)	0.8	0.8
Temperature:		
Cumulative process time at 350°C (hr)	9.5-12.5	6.0-9.0
Cumulative process time at 350-550°C (hr)	12.5-18.5	9.0-15.0
Cumulative process time at 550°C (hr)	18.5-21.5	15.0-16.0

^a Based on the cross sectional area of the reactor and calculated for operating temperature and pressure.

^b Fluorine was introduced through a side inlet (located 6 in. above the bed support of nickel balls) for the first 2 hr and subsequently fed into the bottom of the reactor.

^c Fluorine was introduced through the side inlet for the first 50 min and subsequently fed into the bottom of the reactor.

The concentration of plutonium in the final alumina beds for both runs Pure-17 and Pure-18 was 0.009 w/o, for a single use of the pellet bed. This corresponded to volatilization of 96.4% of the plutonium in the pellet charge. Since the major portions of the recycle-fluorination sequence shown in Figures II-2 and II-3 were the same, it appears that the UF₆ production rates during the uranium fluorination step had little influence on the final plutonium concentrations in these runs. Less than 10% of the plutonium charge was reacted while most of the uranium was being removed; the plutonium concentration in the alumina bed at the start of recycle-fluorination was about 0.2 w/o in both runs. Prior to recycle-fluorination, 98 and 99.9% of the uranium charges in runs Pure-17 and -18, respectively, had been volatilized. Thus, the U/Pu ratios in the alumina beds at the start of recycle-fluorination

differed by a factor of 14 in these two experiments. The U/Pu ratio, however, appeared to have little influence on the plutonium concentration in the final alumina beds.

With fluorine as the fluorinating agent, the two-step processing sequence, as demonstrated in runs Pure-17 and -18, appears to be more promising than the two-zone concept. With the two-step sequence, fluorination of most of the uranium can be carried out at a lower temperature than now appears feasible for two-zone oxidation-fluorination, and at the lower fluorination temperature the presence of cesium fluoride in the initial charge apparently has a negligible effect on plutonium removal. Fluorination at low temperatures by the two-zone oxidation-fluorination method would be limited by low pellet oxidation rates below 400°C.

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FIG. II-2. Uranium and Plutonium Volatilization during Two-Step Separate Oxidation-Fluorination Process: Run Pure-17.

c. FLUORINATION OF $\text{UO}_2\text{-PuO}_2\text{-F.P. PELLETS}$ WITH BrF_5

Operating conditions for experiments with BrF_5 as a selective fluorinating agent for the separation of uranium from uranium-plutonium mixtures, runs Purse-1 to -7, are summarized in Table II-5. In run Purse-1, a 1-in. deep bed of fuel pellets was used to demonstrate the use of BrF_5 as a selective fluorinating agent; the BrF_5 fluorination step was carried out at 400°C , followed by recycle-fluorination at 450 to 550°C . In subsequent runs, Purse-2 to -6, the BrF_5 step was con-

ducted at 300°C and various alternative recycle-fluorination sequences in the temperature range 300 to 600°C were evaluated. A BrF_5 fluorination temperature of 200°C , followed by recycle-fluorination at 200 to 550°C , was investigated in run Purse-7.

(1) Preliminary Experiment with One-inch Deep Bed of Pellets

Uranium and plutonium concentrations in the fluidized alumina bed during run Purse-1 are shown in Figure II-4. After 1.75 hr of reaction with BrF_5 , more

than 99% of the uranium had been volatilized from the alumina bed; an additional 1.25 hr of fluorination increased the uranium volatilization to about 99.8%. To verify that selective fluorination of only the uranium

finer had occurred during the BrF_5 step, samples from the soda lime traps used for disposal of the UF_6 , unreacted BrF_5 , and bromine reaction product were analyzed for plutonium. These samples contained 4×10^{-5} to 9×10^{-5} w/o Pu which, from previous experience with the equipment used in sampling and grinding the soda lime, is known to be the background level of contamination. These data therefore indicated that no plutonium was volatilized during the BrF_5 step. During recycle-fluorination with fluorine, about 0.5 g uranium was volatilized from the alumina bed along with 1.2 g plutonium. It should be possible to reduce the quantity of uranium in the plutonium product by increasing the time of fluorination with BrF_5 or the concentration of BrF_5 .

The concentration of both uranium and plutonium in the final alumina bed was 0.008 w/o for a single use of the alumina bed. These results compare very favorably with concentrations of 0.010 w/o (U and Pu) obtained in run Pure-11 (see Figure II-1) in which a 1-in. bed of pellets was reacted by the two-zone processing cycle. Run Purse-1 showed that the use of BrF_5 as a fluorinating agent is a promising method of reprocessing $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ fuel pellets.

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FIG. II-3. Uranium and Plutonium Volatilization during Two-Step Separate Oxidation-Fluorination Process: Run Pure-18.

TABLE II-5. AVERAGE OPERATING CONDITIONS—RUNS PURSE-1 TO PURSE-7

Equipment: 2-in. dia. fluid-bed reactor $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ Pellets (Type II): Size: 0.5-in. dia. by 0.4-in. right cylinders Weight: ~650 g ^a Bed depth: 2 in. ^a		Alumina Bed: Material: Alcoa T-61 alumina Size Limits: Nominal 48 to 100 mesh (-170 mesh fraction removed) Weight: 1100 g Static bed depth: 12 in. Weight of Cesium Fluoride: 0.6 g Bed Support: Nickel balls Diluent Gas: Nitrogen					
	Purse-1	Purse-2	Purse-3	Purse-4	Purse-5	Purse-6	Purse-7
Oxidation at 450°C							
Cumulative process time (hr)	0-2.0	0-4.0	0-4.0	0-4.0	0-4.0	0-4.0	0-4.0
Reactor pressure (mm Hg)	980	960	950	920	1010	980	990
Superficial gas velocity ^b (ft/sec)	0.8	0.8	0.7	0.8	0.8	0.8	0.8
Oxygen concentration to pellet bed (v/o)	20	20	20	20	19	20	21
Fluorination with BrF_5							
Cumulative process time (hr)	2.0-5.0	4.0-6.0	4.0-5.7	4.0-5.8	4.0-5.8	4.0-6.0	4.0-9.5
Reactor pressure (mm Hg)	960	1170	1130	1130	1080	1140	1200
Superficial gas velocity ^b (ft/sec)	0.8	0.6	0.6	0.7	0.6	0.7	0.6
BrF_5 concentration to fluid bed (v/o)	2-8	5-10	5-10	5-10	11	9	10
Temperature (°C)	400	300	300	300	300	300	200
Fluorination with F_2 (Once-through Flow)							
Cumulative process time (hr)	-	6.0-8.0	-	-	-	-	-
Reactor pressure (mm Hg)	-	1290	-	-	-	-	-
Superficial gas velocity ^b (ft/sec)	-	0.7	-	-	-	-	-
Fluorine concentration to fluid bed (v/o)	-	10	-	-	-	-	-
Temperature (°C)	-	300-550	-	-	-	-	-
Recycle-fluorination with 90 v/o Fluorine							
Cumulative process time (hr)	5.0-17.0	8.0-16.0	5.7-17.7	5.8-20.8	5.8-15.8	6.0-20.0	9.5-25.5
Reactor pressure (mm Hg)	3170	1330	1340	1260	1410	1420	1320
Superficial gas velocity ^b (ft/sec)	0.9	0.5	0.5	0.6	0.7	0.6	0.6
Temperature (°C)	450°C, 5.0-6.0 hr 500°C, 6.0-9.0 hr 550°C, 9.0-17.0 hr	550°C	450°C, 5.7-6.7 hr 500°C, 6.7-9.7 hr 550°C, 9.7-17.7 hr	300°C, 5.8-10.8 hr 300-550°C, 10.8-15.8 hr 550°C, 15.8-18.8 hr 600°C, 18.8-20.8 hr	300°C, 5.8-8.8 hr 300-550°C, 8.8-13.8 hr 550°C, 13.8-15.8 hr	300°C, 6.0-8.0 hr 350°C, 8.0-11.0 hr 400°C, 11.0-14.0 hr 450°C, 14.0-16.0 hr 500°C, 16.0-17.0 hr 550°C, 17.0-20.0 hr	200°C, 9.5-12.5 hr 250°C, 12.5-15.5 hr 300°C, 15.5-18.5 hr 300-550°C, 18.5-23.5 hr 550°C, 23.5-25.5 hr

^aOnly 332 g of pellets, corresponding to a 1-in. bed depth, were used in run Purse-1.

^bBased on the cross-sectional area of the reactor and calculated for operating temperature and pressure.

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FIG. II-4. Course of Uranium and Plutonium Removal during Fluorination with BrF_5 Followed by Fluorine: Run Purse-1.

(2) Investigation of Alternative Recycle-Fluorination Schemes

In runs Purse-2 to -6, alternative recycle-fluorination sequences following a BrF_5 fluorination step at 300°C were evaluated. The recycle-fluorination sequence in run Purse-3 was similar to that used in run Purse-8 and consisted of 1 hr at 450°C , 3 hr at 500°C , and 8 hr at 550°C . The plutonium concentration in the final alumina bed, 0.021 w/o, was less satisfactory than the 0.014 w/o Pu obtained in run Purse-8; thus this recycle-fluorination sequence was not considered to be an effective means for plutonium removal following fluorination of uranium at 300°C with BrF_5 .

In run Purse-2, the plutonium was fluorinated with 10 v/o fluorine while the temperature was raised from 300 to 550°C over 2 hr, followed by recycle-fluorination with 90 v/o fluorine at 550°C for 8 hr. The plutonium concentration in the final alumina bed was also relatively high, 0.028 w/o Pu. Most of the plutonium was volatilized during the first two hours of fluorination; the recycle-fluorination at 550°C had little effect on plutonium removal.

In run Purse-4, recycle-fluorination with 90 v/o fluorine for 5 hr while changing the temperature from 300 to 550°C ($10^\circ\text{C}/12\text{ min}$), following 5 hr of recycle-fluorination at 300°C , proved to be very effective in reducing the plutonium concentration to a low level of 0.006 w/o. Analyses of plutonium in the fluidized bed samples showed that little plutonium volatilized during the final 2 hr at 550°C and during an additional 2 hr at 600°C ; the plutonium concentration in the final alumina bed was 0.0055 w/o. This amounted to 98% removal of the initial plutonium charge for a single use of the alumina bed.

The recycle-fluorination sequence of 15 hr used in run Purse-4 was reduced to 10 hr in run Purse-5. As shown in Figure II-5, the plutonium concentration in the final alumina bed was 0.007 w/o, which compared favorably with that obtained in run Purse-4. The

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FIG. II-5. Course of Uranium and Plutonium Removal during Fluorination with BrF_5 Followed by Fluorine: Run Purse-5.

course of plutonium removal in this run also indicated that the shorter recycle-fluorination sequence was effective for the removal of plutonium from the alumina bed.

A programmed temperature increase in the 2-in. dia. reactor may approximate the thermal lags in response to a rise in control temperature for a large plant-scale reactor, and such a scheme on a laboratory scale may therefore have significance for a recycle-fluorination procedure applied to a full-scale process.

It was observed that during the 5-hr period of programmed temperature increase from 300 to 550°C in runs Purse-4 and -5, the rate of plutonium removal increased significantly at a temperature between 350 to 400°C. Run Purse-6 was therefore carried out with emphasis placed on recycle-fluorination at temperatures less than 450°C. The recycle-fluorination sequence and the uranium and plutonium concentration in the fluidized alumina bed are shown in Figure II-6. Since the plutonium concentration in the final alumina bed (0.006 w/o) is essentially the same as that obtained in run Purse-5, the increased time at temperatures less than 450°C during recycle-fluorination in run Purse-6 did not result in improved plutonium removal.

(3) Effect of Low-Temperature Fluorination with BrF_5

Tests by Gabor *et al*⁵ using oxidized UO_2 pellets have indicated that the lowest practical temperature for the BrF_5 fluorination step is 200°C. Therefore, in run Purse-7, the fluorination of oxidized $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets was demonstrated at 200°C with BrF_5 , and plutonium removal during recycle-fluorination at 200 to 550°C was investigated. Average operating conditions for run Purse-7 are given in Table II-5; uranium and plutonium concentrations in the fluidized alumina bed are shown as a function of processing time in Figure II-7.

Approximately 97% of the uranium was fluorinated during 5.5 hr of operation at 200°C with 10 v/o BrF_5 , corresponding to an average production rate of 14 lb UF_6 /(hr) (sq ft). In comparison, in runs Purse-2 to -6, using ~10 v/o BrF_5 at 300°C, fluorination of 98 to 99% of the uranium was obtained in 1.7 to 2.0 hr, resulting in average production rates of 40 to 45 lb UF_6 /(hr) (sq ft). The utilization of BrF_5 , based on total fluorine, was 8% in run Purse-7, as compared with 28 to 37% in runs Purse-2 to -6.

In run Purse-7, the rate of plutonium removal dur-

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FIG. II-6. Course of Uranium and Plutonium Removal during Fluorination with BrF_5 Followed by Fluorine: Run Purse-6.

ing 6 hr of recycle-fluorination at 200 and 250°C was about 0.1 g Pu/hr. This rate was low as compared with an average rate of 0.27 g Pu/hr obtained for 3 hr at 300°C. The plutonium concentration in the final alumina bed was 0.009 w/o; this result can be compared with 0.006 to 0.007 w/o plutonium obtained in runs Purse-4, -5, and -6 which used a BrF_5 fluorination step at 300°C, followed by recycle-fluorination at temperatures of 300 to 550°C. Therefore, in terms of plutonium retention in the final alumina bed, there appears to be no advantage to conducting the BrF_5 step at 200°C rather than at 300°C.

⁵ This report, Section II.B.2.b.

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FIG. II-7. Course of Uranium and Plutonium Removal during Fluorination with BrF_5 Followed by Fluorine: Run Purse-7.

2. Analysis of Bed Material (J. RIHA, M. J. STEINDLER)

The plutonium retained in the alumina bed material of the fluid-bed fluoride volatility process represents a process loss which must be minimized. While current experiments are in progress to determine empirically the optimum conditions for the conversion of plutonium to the hexafluoride and the volatilization of PuF_6 from the bed, it appears most desirable to obtain information on the mechanisms which lead to the retention of plutonium on the alumina bed material. Further, repeated use of an alumina bed for the processing of several batches of fuel, which has been indicated as necessary

in the process for adequate plutonium recovery makes it desirable to have information on the effects of the process reagents on the alumina. Consequently, an examination of alumina-bed materials from experiments in a 2-in. dia. fluid-bed reactor has been undertaken to determine the variations in physical characteristics of unreacted and reacted alumina, the location of plutonium on alumina, the identification and location of fission products on alumina, and the concentrations of fission products relative to the plutonium concentration on the alumina.

a. PHYSICAL CHARACTERISTICS OF ALUMINA BED MATERIAL

A sieve analysis, using U.S. Standard Sieves and vibrating table, was performed on unreacted Alcoa T-61 alumina (nominal 48-100 mesh material with -170 mesh removed) and on the final bed from run Pure-13 (see section II. A. 1. of this report). The size distributions of the alumina particles are listed in Table II-6. A comparison of the particle size distributions of the two materials indicates that a part of the fluorinated alumina showed slight particle growth while another portion of the alumina showed particle diminution. The production of 0.6 w/o fines in run Pure-13 is comparable to results obtained in attrition tests performed on unreacted alumina (ANL-7125, p. 64). Diminution of Alcoa T-61 alumina is not expected to be a processing problem.

Surface area measurements of the various size fractions of unreacted alumina and of the final bed of Pure-13 were determined by the BET method using a Perkin-Elmer Sorptometer. The surface areas of unreacted and fluorinated alumina together with calculated values for spherical particles are listed in Table II-7.

The results indicate that the fluorination cycle produces a threefold increase in the surface area of the particles. If it is assumed that the increase in surface area is due only to the formation of an aluminum fluoride film on the particles and that 1 w/o of the oxide is converted to fluoride,⁶ calculated values for the surface area of aluminum fluoride vary from 1 m²/g for the +60 mesh fraction to 4 m²/g for the -170 mesh fraction. These results indicate that the alumina particles are not drastically altered in form by use in the fluid bed.

b. COMPOSITION OF ALUMINA BED MATERIAL

The electron probe microanalyzer is being used to determine the location of plutonium and fission products as well as the concentrations of fission products relative to the plutonium concentration on the alumina particles.⁷ Descriptions of the alumina samples examined by this technique are listed in Table II-8.

Samples were mounted in self-setting silver epoxy, Eccobond Conductive Solder Type 57C. Owing to the interference of the silver L β X-ray line with the M α X-ray line of plutonium, however, another suitable mounting material had to be found. Copper-impreg-

TABLE II-6. SIEVE ANALYSIS OF UNREACTED ALUMINA AND USED BED MATERIAL

Mesh Size	Unreacted Alumina ^a (w/o)	Final Bed from Run Pure-13 ^b (w/o)
+60	6.4	10.2
-60+100	70.3	66.5
-100+120	14.4	15.2
-120+170	9.1	7.5
-170	—	0.6

^a Values are the averages for sieve analyses of two batches of Alcoa T-61, nominal 48-100 mesh (-170 mesh fraction removed).

^b The alumina in the charge for run Pure-13 also was Alcoa T-61 nominal 48-100 mesh (-170 mesh fraction removed).

TABLE II-7. SURFACE AREA ANALYSES OF UNREACTED ALUMINA AND FLUORINATED ALUMINA

Mesh Size	Surface Area (m ² /g)		
	Calculated value ^a	Unreacted alumina ^b	Final bed from run Pure-13
+60	0.006	0.022	0.090
-60+100	0.008	0.038	0.112
-100+120	0.011	0.042	0.129
-120+170	0.017	0.067	0.164
-170	0.019	0.097	0.320

^a Calculated from the crystal density of Al₂O₃ and assuming spherical particles.

^b Alcoa T-61, nominal 48-100 mesh with -170 mesh fraction removed.

nated Bakelite, requiring both heat and pressure to set, was tried and proved to be successful. Sample preparation was accomplished by the following procedure: 1) the alumina particles were imbedded in copper-impregnated Bakelite, 2) the particles were polished using 320, 400, and 600 grit Durite paper and 3- μ and 1/4- μ diamond paste, 3) the Bakelite plug was decontaminated using Versene solution, soap solution, and swipes with Kleenex wetted with alcohol, and 4) the exposed surface of the particles was coated with a thin, electrically conductive film of Nivac nickel using vacuum evaporation.

The location of the plutonium and each fission product element was determined by two methods of analysis: X-ray scanning image and X-ray line profile. When the latter method is used, the concentration of each element at each site examined is determined by sweeping the electron beam repeatedly across the same sites and recording the rate of emission of the characteristic X-rays of the elements as a function of distance. An alumina particle chosen at random from

⁶ Reactor Development Program Progress Report, February 1966, ANL-7176, March 23, 1966, p. 66.

⁷ Electron probe microanalysis and interpretation of results by Dr. N. R. Stalica is gratefully acknowledged.

TABLE II-8. ALUMINA SAMPLES EXAMINED BY ELECTRON PROBE MICROANALYSIS

Sample No.	Run No. ^a	Mesh Size	Approximate Pu Concentration ^b (w/o)	Process Conditions
I	Pure-13, Bed Sample No. 5	+100	0.195	{ Oxidation-fluorination at 450°C for 5 hr. Single-zone fluorination at 450°C for 1 hr. Recycle-fluorination at 450°C for 1 hr.
II	Pure-13, Bed Sample No. 5	-140+200	0.195	
III	Pure-13, Bed Sample No. 15	+100	0.070	Same as above with additional recycle-fluorination at 500°C for 3 hr and at 550°C for ½ hr.
IV	Pure-13, Final Bed	-60+100	0.024	{ Same as sample III with additional recycle-fluorination at 550°C for 7½ hr.
V	Pure-13, Final Bed	-170	0.024	
VI	Pure-14, Bed Sample No. 7	+100	0.067	Oxidation-fluorination at 450°C for 3 hr. Single-zone fluorination at 450°C for 1 hr. Recycle-fluorination at 450°C for 1 hr and at 500°C for ½ hr.
VII	Pure-14, Bed Sample No. 11	+100	0.037	Same as VI with additional recycle-fluorination at 500°C for 2½ hr.
VIII	Pure-16, Final Bed	+100	0.033	Oxidation-fluorination at 450°C for 3 hr. Recycle-fluorination 10 v/o N ₂ -90 v/o F ₂ at 450°C for 1 hr. Recycle-fluorination 450-550°C for 6 hr and 550°C for 1 hr.

^a Runs Pure-13, Pure-14, and Pure-16 are described in an earlier section of this report.

^b Nominal analysis of total sample as drawn from fluid-bed reactor. Plutonium content of specific size fraction used in the analysis has not been determined.

sample I was examined by the X-ray scanning image technique for all elements initially present in the fission product mixture. The results indicate that the elements are to be found in a layer less than 2 μ deep, which is part of the surface of the particle. Plutonium X-ray images were made of several other particles, and all indicated the plutonium to be on the surface of the particles.

A particle of sample II and a particle of sample VI were chosen at random and intensity profiles were recorded for all elements. The fission product-to-plutonium mole ratios observed are summarized in Table II-9. Where a fission product element was not detected, the mole ratio indicated is the ratio of plutonium to the minimum concentration detectable for that fission product element.

Intensity profiles of plutonium, zirconium, neodymium, and cesium were also made for a total of 47 particles chosen at random from eight samples. Peak concentrations expressed as mole ratios are summarized in Table II-10. The limits of detection in these tables are based on counting statistics and are reported at the one-sigma level.

Analysis of the data would indicate that:

- 1) The Cs/Pu mole ratios are not indicative of simple compounds.
- 2) No particular significance in terms of compounds which might be formed can be attached to Zr/Pu and Nd/Pu mole ratios.
- 3) The presence of cesium does not significantly affect the distribution of fission products.
- 4) Plutonium appears only where fission products are found, indicating retention of plutonium by fission product fluorides.

To supplement the results of the electron probe analysis, an attempt was made to remove the thin fluoride film from the alumina particles. The -120+170 mesh fraction of the final bed of Pure-13 was tumbled with nickel balls for 24 hr. After tumbling, the alumina was screened and the -325 mesh fraction was collected for X-ray diffraction analysis. Approximately 0.8 g was collected from a starting weight of 58 g. The major component found was alpha alumina. Probable minor components reported were AlF₃ and MF₃; the latter is indicative of a metallic trifluoride. To aid in identifying the minor phase, an X-ray spectrometric analysis was performed on the solid. The following elements were found to be present: Pu, U,

TABLE II-9. FISSION PRODUCT-TO-PLUTONIUM MOLE RATIO ON ALUMINA BED PARTICLE

Element	Pellet ^a	Sample II-1 ^b	Sample VI-3 ^b
Zr	0.8	1.0	2.0
Nd	0.3	0.2	1.0
Ce	0.1	0.1	0.6
Sm	0.1	<0.1	0.6
La	<0.0	<0.0	0.4
Pr	<0.0	0.1	0.4
Eu	<0.0	<0.0	0.3
Ba	<0.0	0.2	0.3
Rh	0.1	0.1	0.3
Pd	—	<0.1	0.3
Cs	0.3 ^c	0.3	—
U	200.0	0.1	<0.2
Sr	0.2	0.1	<0.3
Y	<0.0	<0.1	<0.3
Ru	0.3	0.3	<0.3
In	<0.0	<0.0	<0.2
Ag	<0.0	<0.1	<0.2
Cd	0.1	<0.1	<0.2
Gd	<0.0	<0.0	<0.1

^a Type II pellets were used in the runs which preceded sampling of the alumina beds to obtain samples II and VI; for composition of Type II pellets, see Table II-1.

^b The last number (-1 or -3) is the particle number and corresponds to the particle number used in Table II-10.

^c Cesium was not present in the pellet, but was added to the bed.

Y, Zr, Sr, Rh, Pd, Cs, Ba, La, Ce, and Nd. Estimation of the lattice constants of MF₃ indicated the trifluoride probably to be NdF₃.⁸

Complex formation between PuF₆ and CsF, previously believed to be the mechanism of plutonium retention in the alumina bed, is now thought unlikely. Results of the electron probe analysis (Table II-10) indicate Cs/Pu mole ratios of less than 1. Fluorinations of mixtures of PuO₂ and CsF at 450°C resulted in the formation of a double compound having a Cs/Pu mole ratio of 2.⁹ In two-zone fluorination studies in the 2-in. dia. reactor, retention of plutonium on alumina particles in the presence of CsF was observed, but this effect is as yet unexplained. It should be noted that the formation of eutectic mixtures and compounds of CsF with other fission product fluorides could easily arise in the fluid-bed system. Two such systems for which eutectics or compounds could form within the range of temperatures used for recycle-fluorination are

⁸ X-ray spectrometric analysis and interpretation were performed by R. Schablaske.

⁹ R. L. Jarry, L. J. Anastasia, J. Fischer, L. E. Trevorrow, F. D. Baker, and J. J. Stockbar, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part I. The Fluorination of Uranium Dioxide-Plutonium Dioxide Solid Solutions, ANL-6742, September 1963, p. 15.

TABLE II-10. PEAK CONCENTRATIONS OF FISSION PRODUCTS ON ALUMINA EXPRESSED AS FISSION PRODUCT-TO-PLUTONIUM MOLE RATIOS

Sample No.	Cs/Pu	Zr/Pu	Nd/Pu
I-1	0.1	0.5	0.7
-2	0.2	1.4	0.7
-3	0.3	1.5	0.5
-4	0.1	1.5	0.8
-5	0.2	0.8	0.7
-6	0.1	^a	^a
-7	0.1	1.4	0.2
-8	0.1	1.2	0.2
-9	0.1	2.0	0.3
-10	0.1	1.5	0.1
-11	0.5	2.0	0.2
II-1	0.0	1.4	0.2
-2	^b	^b	^b
-3	0.2	0.7	1.7
-4	0.1	1.0	0.7
-5	0.6	1.0	0.8
-6	0.1	0.6	0.7
III-1	0.3	1.7	0.9
-2	0.2	1.4	1.0
-3	0.3	2.4	1.5
-4	^b	^b	^b
-5	1.3	2.4	1.7
IV-1	0.8	0.7	1.2
-2	0.4	1.0	0.3
-3	0.9	^b	0.8
-4	^b	^b	^b
-5	^b	^b	^b
-6	^b	^b	^b
V-1	^b	^b	^b
-2	^b	^b	^b
-3	^b	^b	^b
-4	^b	^b	^b
-5	^b	^b	^b
-6	0.4	0.5	0.6
VI-1	^c	^b	^b
-2	^c	^b	^b
-3	^c	2.3	1.1
VII-1	^c	^b	^b
-2	^c	^b	^b
-3	^c	^b	^b
-4	^c	^b	^b
-5	^c	2.6	0.4
VIII-1	0.2	0.7	0.5
-2	0.6	0.9	0.8
-3	^b	^b	^b
-4	0.3	1.6	0.7
-5	^b	0.8	0.5

^a Not analyzed for.

^b Not detectable.

^c Not analyzed for because cesium was not added to the bed in the run represented by this sample.

CsF-ZrF₄¹⁰ and CsF-AlF₃.¹¹ Interaction between PuF₄ plutonium from mixtures containing cesium.

Experiments were performed using ZrF₄ as an inert and these systems could account for low removals of bed material and resulted in very poor plutonium removals, indicating interaction between ZrF₄ and PuF₄ or between ZrF₄ and PuF₆ (ANL-6379, p. 137). Since PuF₄ and ZrF₄ are isomorphous,¹² the formation of a solid solution is possible, and X-ray diffraction analysis of reaction products from the fluorination of 1:1 mole ratio mixtures of PuO₂ and ZrO₂ confirmed the formation of a solid solution.⁹ Data from the electron probe analysis also yield Zr/Pu ratios of about 1, indicating a possible cause of plutonium retention.

Results of other experiments showed that the rare

earth fluorides can probably be removed from consideration as important factors affecting plutonium removal. Fluorinations at 450°C performed with individual binary mixtures of PuF₄ with LaF₃, PrF₃, or NdF₃ showed no interaction with plutonium.⁹

Based on the evidence presented, it is probable that future investigations of the nature of plutonium retention on alumina bed material will be directed toward: (1) elucidation of the interaction of PuF₄ with low-melting solids which contain fission products, (2) the sintering of such low-melting compounds, (3) the formation of solid solutions of PuF₄ and fission product fluorides, and (4) the sorption of PuF₆ on alumina or the fluoride film.

3. The Reactions of Bromine Pentafluoride (R. L. JARRY, J. STOCKBAR)

Bromine pentafluoride is being considered as a fluorinating agent for use in the fluid-bed reprocessing of spent fuel from nuclear power reactors. The reaction of BrF₅ with mixtures of uranium and plutonium oxides or fluorides converts the uranium to volatile UF₆ while converting the plutonium to the nonvolatile PuF₄ which therefore permits a separation of uranium from plutonium in a single step. In a second step, elemental fluorine is used to convert the PuF₄ to volatile PuF₆.

Previously reported investigations of the reactions of BrF₅ (ANL-7055, pp. 114-122, ANL-7125, pp. 66-73) included:

1. Preliminary kinetic data for the reactions between BrF₅ and UF₄ and between BrF₅ and UO₂F₂.
2. Data for the reaction between BrF₅ and UO₂F₂-UF₄-alumina-nonradioactive fission product mixtures and between BrF₅ and U₃O₈-alumina-nonradioactive fission product mixtures. Reaction conditions were determined which would achieve conversion to UF₆ of greater than 99% of the uranium in such mixtures. Also studied was the effect on uranium removal of the addition to these mixtures of decladding products (from reactions of either Zircaloy or stainless steel cladding with HF-oxygen mixtures).
3. Comparison of the reactivity of BrF₅ with that of fluorine toward mixtures of the types described in item 2.
4. Reaction of mixtures containing U₃O₈ and PuO₂

with BrF₅ to demonstrate that plutonium would not be volatilized under conditions that would result in conversion of greater than 99% of the uranium to UF₆.

This report presents the results of studies of the kinetics of the reaction of BrF₅ with UF₄, UO₂F₂, and U₃O₈. Both thermobalance and boat experiments were performed.

a. EXPERIMENTAL

Materials. The UF₄, UO₂F₂, and U₃O₈ used in these studies were characterized in previous reports (ANL-7055, p. 115, ANL-7125, p. 67). The BrF₅ was obtained from a commercial source and was stated to have a purity of at least 98%. Nitrogen used to dilute the BrF₅ was obtained from liquified gas, and was passed through a Linde Type 4A Molecular Sieve prior to use in order to remove water.

Apparatus. The Sartorius thermobalance used in this work was previously described by Johnson and Fischer.¹³ Briefly, the thermobalance consists of a vertical tubular reactor 1½ in. in dia. and 20 in. long, and a Sartorius Rapid 200 analytical balance equipped with an optical-electronic weight sensing system and a remote recording output. The sample of UF₄ or other solid reactant was placed on a small nickel sample pan about ¾ in. in dia. which was suspended below the balance pan by a Monel chain that hung through an aperture in the top of the reactor. The sample pan was positioned at about the midpoint of the heated portion of the tubular reactor. A chromel-alumel thermocouple in a nickel sheath, placed about ⅛ in. below the sample pan, sensed the reaction temperature. The BrF₅ wa

¹⁰ G. D. Robbins, R. E. Thoma, and H. Insley, J. Inorg. Nucl. Chem. **27**, 559-68 (1965).

¹¹ J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, John Wiley and Sons, New York, 1961, p. 307.

¹² W. H. Zachariasen, Acta Cryst. **2**, 388-90 (1949).

¹³ C. E. Johnson and J. Fischer, J. Phys. Chem. **65**, 1849 (1961).

metered through a rotameter constructed of Kel-F,¹⁴ and the nitrogen used to dilute the BrF₅ was metered by a glass rotameter. The BrF₅ container was maintained at about 50°C, resulting in a pressure at the rotameter of about 1000 torr. The concentration of BrF₃ in the BrF₅ reagent was not known, but was thought to be of the order of <2 m/o. According to the liquid-vapor equilibria data of Long¹⁵ for the BrF₃-BrF₅ system at 50°C and a pressure of ~1000 torr, the vapor phase in equilibrium with the liquid would contain 99 m/o BrF₅, even if the liquid phase contained as much as 15 m/o BrF₃ as an impurity. All of the connecting lines and the BrF₅ rotameter were maintained at a temperature of 70°C. The gaseous mixture of BrF₅ and nitrogen passed through a section of nickel tubing coiled around the outside of the reactor tube; the nickel tubing acted as a preheater for the mixture entering the bottom of the reactor.

The top of the reactor was maintained at a pressure slightly less than the inlet pressure of the reactor by pumping on the outlet line. A nitrogen bleed stream was brought into a chimney attached to the top of the reactor tube just above the vacuum exit to prevent any reactive gas from escaping from the open top of the reactor. The reagent gases and products were drawn off through the outlet line and passed through a trap containing soda lime. Soda lime at 100°C was found to be a satisfactory reactant for disposing of BrF₅ and UF₆, since all components of the mixture are converted to nonvolatile solids.

The boat reactor apparatus used in this work consisted of a horizontal tubular reactor, a gas-metering manifold, and a general purpose manifold to which a system of cold traps and vacuum services was attached. The manifolds were constructed of nickel tubing and fittings. The valves were Hoke 413 Series Monel with nickel diaphragms. The tubular reactor was constructed of a 1-ft length of 2-in. schedule 40 nickel pipe, flanged at one end. A nickel boat (4 in. long, 1 $\frac{3}{8}$ in. wide, and $\frac{3}{16}$ in. deep) contained the solid reactant. A hemicylindrical nickel bar, with a cross section one-half that of the reactor, was placed in the reactor to act as a support for the nickel reaction boat and to distribute heat evenly to the bottom of the boat. The temperature of the boat was sensed by a chromel-alumel thermocouple placed in a well within the bar at the midpoint of the boat and approximately $\frac{1}{16}$ in. from the top surface of the bar.

Procedure. In the thermobalance experiments, the particulate sample (about 300 mg) was weighed in the sample pan and placed in the reactor; then nitrogen flow was started. After the reaction temperature was reached, the BrF₅ flow was started. The reaction continued for 60 min or, at the higher temperatures employed, for a shorter time. The recorded weight change of the loaded sample pan and the reaction time were used to determine the fraction of UF₄ converted to UF₆ during any increment of reaction time.

In the boat reactor experiments, a weighed sample (about 5 g) was placed in the reaction boat to form a uniform layer over the bottom of the boat. The boat was placed in the reactor, and the reactor was then closed and evacuated for leak testing. While the system was being heated, nitrogen at a flow rate of about 200 ml/min was passed through the reactor. When the specified temperature was reached, flow of BrF₅ was started. The linear velocity of the gas phase was about 1.2 cm/sec at a total volume flow rate of about 500 ml/min. The exit gases from the reactor were passed through a trap containing heated soda lime to remove bromine fluorides and UF₆ before being exhausted to the ventilation system. After the reaction was completed, the BrF₅ flow was stopped and the reactor was cooled to room temperature under an atmosphere of flowing nitrogen. The reaction boat was removed from the reactor and weighed to determine the weight loss of the contents of the boat due to reaction.

In both types of experiments, the BrF₅ storage vessel was weighed before and after the reaction period to determine the weight of BrF₅ used.

b. RESULTS AND DISCUSSION

The rate data were treated using the "diminishing sphere" model developed by Anderson.¹⁶ In this kinetic model, the reaction rate is related to the changing surface area available for reaction as a function of the reduction in diameter of the solid particles with reaction time. The final equation developed is:

$$(1 - F)^{1/3} = 1 - k't$$

in which F is the fraction of the solid reacted in time t , and k' is a reaction rate constant. The rate constant k' is related to the true rate constant, k , by the expression

$$k' = k/r_o\rho_o$$

in which r_o is the initial radius of the particle and ρ_o is the bulk density of the solid.

UF₄-BrF₅ Reaction. A series of thermobalance experiments were performed to determine the effect of the

¹⁴ A polymer of chlorotrifluoroethylene. Flowmeter manufactured by Brooks Instrument Div. of Emerson Electric, Attfield, Pa.

¹⁵ R. D. Long, The Liquid-Vapor Equilibria of the System Bromine Pentafluoride-Bromine Trifluoride, ANL-5405, March 1955.

¹⁶ J. S. Anderson, Bull. Soc. Chim. France **20**, 781 (1953).

sample size on the reaction rate constant for the $\text{BrF}_5\text{-UF}_4$ reaction. The reaction temperature was 235°C , and the quantity of UF_4 used varied from 100 to 500 mg. A BrF_5 partial pressure of 243 torr and a gas phase linear velocity of 0.64 cm/sec were employed. The results obtained showed a decreasing value for the rate constant, k' , with increasing initial quantity of UF_4 used in the experiments. Values of the rate constant were 11.5, 9.28, 9.57, and $6.33 \times 10^{-3} \text{ min}^{-1}$ for UF_4 quantities of 100, 200, 300, and 500 mg, respectively. A quantity of 300 mg of UF_4 was selected as the sample size for use in the kinetic experiments.

Thermobalance experiments were performed to determine the effect of the linear velocity of the gas phase on the reaction rate constant. The reactions were performed at 235°C using a gas phase containing 32 v/o BrF_5 (partial pressure of 243 torr) and 68 v/o nitrogen. The values of the rate constant obtained at linear velocities of 0.46, 0.64, and 1.28 cm/sec were 6.62 , 6.33 , and $5.80 \times 10^{-3} \text{ min}^{-1}$, respectively. These

TABLE II-11. REACTION RATE CONSTANTS, k' ,
FOR THE $\text{UF}_4\text{-BrF}_5$ REACTION
Linear velocity of gas phase, 0.64 cm/sec;
 UF_4 sample size, 300 mg.

Temperature (°C)	Rate Constant $k' \times 10^3 \text{ (min}^{-1}\text{)}$		$(k'_{\text{calc.}} - k'_{\text{exp.}}) \times 10^3 \text{ (min}^{-1}\text{)}$
	Exp.	Calc. ^a	
A. $P_{\text{BrF}_5} = 138 \text{ torr. (18 v/o BrF}_5, 82 \text{ v/o N}_2)$ $\log k' = 5.157 - 3720/T$			
200	1.97	1.98	+0.01
225	4.92	4.92	0.00
250	11.3	11.2	-0.1
274	22.7	22.9	+0.2
B. $P_{\text{BrF}_5} = 239 \text{ torr. (31 v/o BrF}_5, 69 \text{ v/o N}_2)$ $\log k' = 5.181 - 3690/T$			
200	2.42	2.45	+0.03
210	3.62	3.55	-0.07
230	6.87	7.14	+0.27
240	10.4	9.9	-0.5
262	19.0	19.6	+0.6
274	28.2	27.7	+0.5
C. $P_{\text{BrF}_5} = 370 \text{ torr. (49 v/o BrF}_5, 51 \text{ v/o N}_2)$ $\log k' = 5.185 - 3650/T$			
199	2.82	2.84	+0.02
219	5.90	5.85	-0.05
234	10.0	9.69	-0.31
249	15.2	15.6	+0.4
260	22.2	21.8	-0.4

^a Values in this column were calculated by use of the equations in headings A, B, and C.

results show only a 13 % change in the rate constant for a nearly threefold increase in the linear velocity. A linear velocity of 0.64 cm/sec was chosen for subsequent thermobalance experiments with UF_4 .

Kinetic data for the $\text{UF}_4\text{-BrF}_5$ reaction were determined over the nominal temperature range 200 to 275°C and a BrF_5 partial pressure range of 138 to 370 torr (corresponding to BrF_5 concentrations of 18 to 49 v/o). The reaction conditions and the values of the rate constant are listed in Table II-11. The effect of temperature on the rate constant is shown in Figure II-8. The integrated form of the Arrhenius equation was fitted to the data by the method of least squares, resulting in the equations listed in Table II-11 which represent the temperature dependence of the reaction rates. Values of the apparent activation energy were 17.0, 16.9, and 16.7 kcal/mole for BrF_5 partial pressures of 138, 239, and 370 torr, respectively.

Values of the rate constant were calculated at selected temperatures, and the values are shown in Figure II-9 as plots of $\log k'$ versus $\log$ partial pressure of BrF_5 . Values of the coefficient, n , of the pressure term of the equation $k' = Ae^{-E/RT}P^n$ were calculated using the slopes of the plots in Figure II-9. The values of n obtained ranged from 0.36 to 0.40. Averaging the constants for the Arrhenius equations and using the average value of the coefficient, n , the following equation was derived to represent the simultaneous temperature and pressure dependence of the rate constant for the $\text{UF}_4\text{-BrF}_5$ reaction:

$$\log k' = 4.286 - 3690/T(^{\circ}\text{K}) + 0.38 \log P_{\text{BrF}_5} (\text{torr}).$$

The activation energy calculated using the above equation is 16.9 kcal/mole.

The reaction between UF_4 and BrF_5 is complicated by the formation of intermediate fluorides, U_2F_9 , U_4F_{17} , UF_6 , either as the result of the direct reaction or by the interaction of UF_6 with UF_4 . The possible reactions, using UF_6 as the example of the intermediate fluoride, are as follows:

Although the color of the reaction residues, either brown or black, indicated the presence of the intermediate compounds, no evidence of an induction period in the weight change of the samples was observed. Evidently the reaction to form volatile UF_6 does not require the formation of significant quantities of the intermediate fluorides. Hence, the reaction is believed to proceed by

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FIG. II-8. Temperature Dependence of the Rate Constant for the $\text{UF}_4\text{-BrF}_5$ Reaction.

UF_4 sample size: 300 mg

Linear velocity of gas phase: 0.64 cm/sec

direct conversion of UF_4 to UF_6 . The reaction of UF_4 with fluorine has been shown to proceed in a similar manner. Labaton and Johnson¹⁷ have demonstrated that the $\text{UF}_4\text{-F}_2$ reaction did not proceed through a step involving the formation of intermediate fluorides, but rather proceeded by the direct fluorination of UF_4 to UF_6 . These workers also showed that the rate of fluorination of the intermediate fluorides was lower by factor of 2 to 4 than the rate of fluorination of UF_4 .

¹⁷ V. Y. Labaton and K. D. B. Johnson, *J. Inorg. Nucl. Chem.* **10**, 74 (1959).

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FIG. II-9. Effect of BrF_5 Partial Pressure on the Rate Constant for the $\text{UF}_4\text{-BrF}_5$ Reaction.

It is assumed that these relative rates are valid for the fluorination reaction with BrF_5 as well.

The equations listed above show bromine as a reaction product. Bromine was indicated by the deep red color of the condensed reaction products and was quantitatively assayed by conversion of bromine to BrF_3 using the fluorine titration method of Sheft and coworkers.¹⁸ Fluorine titrations of the condensed products from several experiments showed quantities of Br_2 corresponding to the stoichiometry of reaction 1 above. Bromine could result from the direct reduction of BrF_5 to Br_2 or from the stepwise reduction to BrF_3 which, in turn, would react further to form Br_2 . In either case, the observed kinetics would be those for the $\text{UF}_4\text{-BrF}_5$ reaction if the rate of the $\text{UF}_4\text{-BrF}_3$ reaction is higher than that for the $\text{UF}_4\text{-BrF}_5$ reaction. Since no data are available in the literature for the reaction between UF_4 and BrF_3 , boat reactor experiments were performed to obtain rate data at 200°C for the two

¹⁸ I. Sheft, H. H. Hyman, and J. J. Katz, *Anal. Chem.* **25**, 1877 (1953).

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FIG. II-10. UO_2F_2 - BrF_5 Reaction at 250°C: Effect of BrF_5 Partial Pressure on the Conversion of Uranium to UF_6 .

Sample size: 5 g

Velocity: 0.86 cm/sec

reactions. For the UF_4 - BrF_5 reaction at a BrF_5 partial pressure of 198 torr, the rate constant was 0.00235 min^{-1} , while for the UF_4 - BrF_3 reaction at a BrF_3 partial pressure of 105 torr, the rate constant was 0.0145 min^{-1} . These data show clearly that the reaction rate with BrF_3 is significantly higher, and therefore, the kinetics measured represent the reaction with BrF_5 .

Comparison of BrF_5 , ClF_3 , and F_2 as Fluorinating Agents for UF_4 . The value of the activation energy, 16.9 kcal/mole, found for the UF_4 - BrF_5 reaction is in the range of values reported in Ref. 17 and ANL-5896 for the UF_4 - F_2 reaction, 14 to 20 kcal/mole, rather than in the 2 to 6 kcal/mole range reported for the UF_4 - ClF_3 reaction.^{19, 20} The order of the UF_4 - BrF_5 reaction was found to be fractional with respect to BrF_5 pressure, while the order of both the UF_4 - F_2 ¹⁷ and UF_4 - ClF_3 ¹⁹ reactions was found to be unity with respect to the partial pressure of the fluorinating agents. Finally, the temperature dependence of the rate of the UF_4 - BrF_5 reaction did not show a minimum as was observed for the UF_4 - ClF_3 reaction;¹⁹ the latter was ascribed to the formation of intermediate fluorides and a consequent reduction in the rate of volatilization of UF_6 .

UO_2F_2 - BrF_5 Reaction. The overall reaction between UO_2F_2 and BrF_5 is considered to proceed as shown in the

¹⁹ V. Y. Labaton, J. Inorg. Nucl. Chem. **10**, 86 (1959).

²⁰ W. Davis, Jr. and R. L. Jarry, Reactions of Gaseous Chlorine Trifluoride with Uranium Tetrafluoride, K-849, Dec. 18, 1953.

TABLE II-12. EXPERIMENTAL AND CALCULATED REACTION RATE CONSTANTS, k' FOR THE UO_2F_2 - BrF_5 REACTION
Linear velocity of gas phase, 0.86 cm/sec;
 UO_2F_2 sample size, 5 g.

Temperature (°C)	Rate Constant $k' \times 10^3 \text{ (min}^{-1}\text{)}$		$(k'_{\text{calc.}} - k'_{\text{exp.}}) \times 10^3 \text{ (min}^{-1}\text{)}$
	Exp.	Calc. ^a	
A. $P_{\text{BrF}_5} = 130 \text{ torr. (17 v/o BrF}_5, 83 \text{ v/o N}_2\text{)}$ $\log k' = 1.561 - 1850/T$			
200	4.30	4.57	+0.27
225	7.42	7.17	-0.25
250	11.6	10.8	-0.8
275	15.9	15.6	-0.3
300	20.5	21.9	+1.4
B. $P_{\text{BrF}_5} = 197 \text{ torr. (30 v/o BrF}_5, 70 \text{ v/o N}_2\text{)}$ $\log k' = 1.484 - 1740/T$			
175	4.04	3.99	-0.05
200	5.97	6.41	+0.44
225	10.5	9.8	-0.7
250	13.1	14.4	+1.3
275	21.2	20.4	-0.8
300	27.6	28.1	+0.5
C. $P_{\text{BrF}_5} = 357 \text{ torr. (47 v/o BrF}_5, 53 \text{ v/o N}_2\text{)}$ $\log k' = 1.848 - 1830/T$			
212	10.4	11.7	+1.3
225	16.9	14.7	-2.2
250	21.9	22.0	+0.1
275	32.0	31.8	-0.2
300	43.2	44.5	+1.3

^a Values in this column were calculated by use of the equations in headings A, B, and C.

following equation:

In this reaction, as was shown for the UF_4 - BrF_5 reaction, Br_2 is postulated as a reaction product of the BrF_5 component of the reaction.²¹ The instability of bromine oxides at temperatures above 0°C²² makes their presence highly improbable.

Thermobalance experiments were performed to determine the fraction of UO_2F_2 converted to UF_6 at several time intervals, temperatures, and BrF_5 partial pressures. The data were treated using the diminishing-sphere model. Values of the function $(1 - F)^{1/3}$ are

²¹ See section II.A.3. of this report on the U_3O_8 - BrF_5 reaction in which it was shown that Br_2 is also the only bromine bearing product of the BrF_5 component in that reaction.

²² M. Schmeisser and K. Brandle, *Advances in Inorganic and Radiochemistry*, Vol. 5, Academic Press, New York, 1963, p. 70.

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FIG. II-11. Temperature Dependence of the Rate Constant for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ Reaction.

Sample size: 5 g

Velocity: 0.86 cm/sec

plotted against reaction time t in Figure II-10, for reactions performed at 250°C and BrF_5 partial pressures of 130, 197, and 357 torr. The lines drawn through the data in Figure II-10 represent the least squares equations, from which values of the rate constant, k' , of 0.0116, 0.0131, and 0.0219 min^{-1} were calculated for partial pressures of BrF_5 of 130, 197, and 357 torr, respectively.

Values of the rate constant, calculated as described above, for data obtained in the nominal temperature range 175 to 300°C and at partial pressures of BrF_5 of 130, 197, and 357 torr, are listed in Table II-12 and shown in Figure II-11. The integrated form of the Arrhenius equation was fitted to the data by the method of least squares; the equations obtained are listed in Table II-12, along with values of k' calculated using these equations. Calculated values of the apparent activation energy are 8.4, 8.3, and 8.0 kcal/mole, for BrF_5 partial pressures of 130, 197, and 357 torr, respectively.

Values of the rate constant were calculated at selected temperatures and the values are shown as plots of $\log k'$ versus $\log$ partial pressure of BrF_5 in Figure II-12. Values of the coefficient, n , of the pressure term of the equation $k' = Ae^{-E/RT}P^n$ were calculated using the slope of the plots of Figure II-12. The values obtained ranged from 0.70 to 0.71. The following equation was derived

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FIG. II-12. Effect of BrF_5 Partial Pressure on the Rate Constant for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ Reaction.

to represent the simultaneous temperature and pressure dependence of the rate constant for the $\text{UO}_2\text{F}_2\text{-BrF}_5$ reaction:

$$\log k' = -\frac{1810}{T(^{\circ}\text{K})} + 0.71 \log P_{\text{BrF}_5} (\text{torr}).$$

The activation energy calculated using the above equation is 8.3 kcal/mole.

The effect of the linear velocity of the gas phase upon the rate constant was investigated in a series of thermobalance experiments performed at 250°C with a BrF_5 partial pressure of 197 torr. Values of the rate constant were 0.0135, 0.0131, and 0.0122 min^{-1} at gas phase linear velocities of 0.86, 1.28, and 2.92 cm/sec, respectively. These results show less than a 10% change in the rate constant for a greater than threefold increase in the linear velocity, indicating a small effect of the linear velocity on the rate constant.

Comparison of BrF_5 , ClF_3 , F_2 , and SF_4 as Fluorinat-

TABLE II-13. EFFECT OF LINEAR VELOCITY OF GAS PHASE ON THE REACTION RATE CONSTANT FOR THE U_3O_8 - BrF_5 REACTION

Total system pressure: 760 torr
Quantity of U_3O_8 used: 300 mg

Reaction Temperature (°C)	Linear Velocity (cm/sec)	Rate Constant, $k' \times 10^3$ (min ⁻¹)
A. $P_{BrF_5} = 108$ torr (14 v/o BrF_5 -86 v/o N_2)		
277	0.61	9.67
276	1.28	9.66
275	1.92	9.55
B. $P_{BrF_5} = 189$ torr (25 v/o BrF_5 -75 v/o N_2)		
243	0.67	8.03
243	1.31	7.90
C. $P_{BrF_5} = 369$ torr (49 v/o BrF_5 -51 v/o N_2)		
256	0.43	20.0
255	0.67	19.6
254	0.88	19.3

ing Agents for UO_2F_2 . Previous studies of fluorinations of UO_2F_2 include the reaction with ClF_3 ,^{23, 24} with fluorine (Ref. 25 and ANL-5959), and with SF_4 .¹³ Activation energies for these reactions are ClF_3 , 8.9 kcal/mole;²⁴ fluorine, 19.5 kcal/mole (ANL-5959); and SF_4 , 32 kcal/mole.¹³ The dependence of the rate constant on the partial pressure of the fluorinating gas was found to be first order for the UO_2F_2 - ClF_3 reaction²⁴ and proportional to the 1.5 power for the UO_2F_2 - SF_4 reaction.¹³ The present investigation of the UO_2F_2 - BrF_5 reaction showed an activation energy of 8.3 kcal/mole and an order of pressure dependence of 0.71, which is similar to those found for the UO_2F_2 - ClF_3 reaction rather than those found for the UO_2F_2 - SF_4 reactions.

U_3O_8 - BrF_5 Reaction. The Sartorius thermobalance was used in the study of the kinetics of the U_3O_8 - BrF_5 reaction. Experiments were performed in the temperature range 225 to 360°C, a BrF_5 partial pressure range of 89 to 369 torr, and a gas phase linear velocity of 0.4 to 2.0 cm/sec. The total system pressure was about one atmosphere.

The reaction between U_3O_8 and BrF_5 is considered by analogy to the U_3O_8 -fluorine reaction to proceed ac-

ording to the following equations:

In addition, as reported by Rampy,²⁶ U_3O_8 reacts with UF_6 to form UO_2F_2 and UF_4 as shown in the following equation:

Evidence for the reaction between U_3O_8 and UF_6 was reported for boat reactor experiments in the previous semiannual report (ANL-7125, pp. 66-73).

In Equations 1 and 2 above, bromine is given as a reaction product of the BrF_5 component of the reaction. This was verified by fluorine titration of the bromine in the condensed reaction products, the technique used for analysis of the UF_4 - BrF_5 reaction products. Determination of the bromine content of the condensed products from five experiments resulted in an average value of $102 \pm 4\%$ of the stoichiometric quantity of bromine; individual values ranged from 94 to 108%. The stoichiometric quantity of bromine was calculated from the fraction of U_3O_8 converted to UF_6 in each experiment, based on the stoichiometry of reactions 1 and 2.

The analytical method was tested by titrating synthetic reaction product mixtures containing only bromine and BrF_5 . The quantity of bromine added to the BrF_5 was determined from PVT relationships. Three synthetic mixtures were titrated and resulted in an average value of $100 \pm 7\%$ of the theoretical amount of bromine, with individual values of 94, 97, and 108%. These results show that the U_3O_8 - BrF_5 reaction data fall within the precision of the analytical method, and indicate that bromine is the only bromine-bearing product of the reaction.

Experiments were performed to determine the effect of different linear velocities of the gas phase on the reaction rate constant for the U_3O_8 - BrF_5 reaction. Three sets of experiments were performed, at BrF_5 partial pressures of 108, 189, and 369 torr, and the results are listed in Table II-13. These results indicate that the effect of linear velocity of the gas phase on the rate constant is negligible.

The kinetics of the U_3O_8 - BrF_5 reaction were determined at BrF_5 partial pressures of 89, 108, 189, 241, and 369 torr, and in the nominal temperature range 225 to 360°C. The values of the rate constant are listed in Table II-14 and plotted in Figure II-13. Also listed in Table II-14 are equations derived by least square fitting of the Arrhenius equation to the data. Th

²³ J. F. Ellis and C. W. Forrest, J. Inorg. Nucl. Chem. **16**, 150 (1960).

²⁴ R. W. Levin, V. G. Katzel, R. F. Smith, Paducah Plant Laboratory Quarterly Progress Report, January-March 1964, KY-L-362, Part 1, 1964.

²⁵ G. Vandenbussche and T. Kekendai, Compt. Rend. **256**, 4657 (1963).

²⁶ G. A. Rampy, Fluorination of Recovery Oxide, GAT-L-366, June 5, 1957.

TABLE II-14. EXPERIMENTAL AND CALCULATED RATE CONSTANTS, k' , FOR THE U_3O_8 - BrF_5 REACTION

Temperature (°C)	Rate Constant, $k' \times 10^3$ (min ⁻¹)		$(k'_{\text{Calc.}} - k'_{\text{Exp.}})$ $\times 10^3$ (min ⁻¹)
	Exp.	Calc. ^a	
A. $P_{\text{BrF}_5} = 89$ torr (12 v/o BrF ₅ -88 v/o N ₂) $\log k' = 1.516 - 2000/T$ Linear Velocity: 0.76 cm/sec			
252	4.80	5.14	+0.34
267	7.04	6.56	-0.48
278	8.60	7.78	-0.82
313	10.3	12.8	+2.50
327	16.3	15.4	-0.90
358	23.5	22.4	-1.10
B. $P_{\text{BrF}_5} = 108$ torr (14 v/o BrF ₅ -86 v/o N ₂) $\log k' = 1.892 - 2130/T$ Linear Velocity: 0.61 cm/sec			
253	7.10	6.88	-0.22
261	8.40	7.92	-0.48
275 ^b	9.55	10.0	+0.45
276 ^c	9.66	10.0	+0.34
277	9.67	10.3	+0.63
298	14.0	14.4	+0.40
316	18.4	18.7	+0.30
329	22.7	22.4	-0.30
C. $P_{\text{BrF}_5} = 189$ torr (25 v/o BrF ₅ -75 v/o N ₂) $\log k' = 1.926 - 2080/T$ Linear Velocity: 0.67 cm/sec			
243	8.03	7.82	-0.21
243 ^d	7.90	7.82	-0.08
244	7.70	7.96	+0.26

Temperature (°C)	Rate Constant, $k' \times 10^3$ (min ⁻¹)		$(k'_{\text{Calc.}} - k'_{\text{Exp.}})$ $\times 10^3$ (min ⁻¹)
	Exp.	Calc. ^a	
C. $P_{\text{BrF}_5} = 189$ torr (25 v/o BrF ₅ -75 v/o N ₂) $\log k' = 1.926 - 2080/T$ Linear Velocity: 0.67 cm/sec—Continued			
262	10.7	10.9	+0.20
278	15.1	14.1	-1.00
286	14.5	16.0	+1.50
301	20.4	20.0	-0.40
302	20.7	20.3	-0.40
D. $P_{\text{BrF}_5} = 241$ torr (32 v/o BrF ₅ -68 v/o N ₂) $\log k' = 1.809 - 1940/T$ Linear Velocity: 0.64 cm/sec			
226	8.44	8.48	+0.04
252	13.2	13.2	0.00
257	14.9	14.3	-0.60
278	18.7	19.7	+1.00
302	28.2	27.6	-0.60
E. $P_{\text{BrF}_5} = 369$ torr (49 v/o BrF ₅ -51 v/o N ₂) $\log k' = 1.813 - 1860/T$ Linear Velocity: 0.67 cm/sec			
223	11.5	11.5	0.00
239	14.9	15.0	+0.10
254 ^e	19.3	19.2	-0.10
255	19.6	19.5	-0.10
256 ^f	20.0	19.8	-0.20
272	24.7	25.0	+0.30
299	36.4	36.4	0.00

^a Values in this column were calculated by use of equations in headings A, B, C, D, and E.

^b Linear velocity of gas phase: 1.92 cm/sec.

^c Linear velocity of gas phase: 1.28 cm/sec.

^d Linear velocity of gas phase: 1.31 cm/sec.

^e Linear velocity of gas phase: 0.88 cm/sec.

^f Linear velocity of gas phase: 0.43 cm/sec.

lines drawn through the data points in Figure II-13 represent the equations. From the slopes of these lines, values of the activation energy of 9.1, 9.8, 9.5, 8.9, and 8.5 kcal/mole were calculated for data obtained at 89, 108, 189, 241, and 369 torr, respectively.

Values of the rate constant at selected temperatures, calculated using the equations listed in Table II-14, are plotted in Figure II-14 as $\log k'$ versus the log of the BrF_5 partial pressure. Values of the pressure dependence of the reaction were calculated from the slopes of the plots of Figure II-14 and ranged in value from 0.87 to 0.93 with an average value of 0.90. From these data, the following equation was derived for the combined temperature and pressure dependence of the U_3O_8 - BrF_5 reaction:

$$\log k' = 0.90 \log P_{BrF_5} (\text{torr}) - 2000/T(^{\circ}\text{K}) - 0.220$$

A value of 9.2 kcal/mole was calculated for the activation energy for the combined data.

The activation energy for the U_3O_8 - BrF_5 reaction falls between the value of 21.3 kcal/mole found for the reaction of U_3O_8 with fluorine²⁷ and the value of approximately 1 kcal/mole found for the reaction of U_3O_8 with BrF_3 .²⁸ The pressure dependence of all these reactions is approximately first order. In contrast to the U_3O_8 - BrF_3 reaction, the U_3O_8 - BrF_5 reaction did not exhibit a minimum in the temperature dependence of the rate constant.

²⁷ M. Iwasaki, J. Inorg. Nucl. Chem. **26**, 1853 (1964).

²⁸ M. Iwasaki and T. Sakurai, J. Nucl. Sci. Tech. (Tokyo) **2**, 225 (1965).

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FIG. II-13. Temperature Dependence of the Rate Constant for the U_3O_8 - BrF_5 Reaction. U_3O_8 Sample: 300 mg

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FIG. II-14. Effect of BrF_5 Partial Pressure on the Rate Constant for the U_3O_8 - BrF_5 Reaction.

4. Condensed Phase Equilibria in the System MoF_6 - UF_6 (L. TREVORROW, D. STEIDL)

A study of the solid-liquid equilibria in the system UF_6 - MoF_6 has been completed. Temperatures of thermal arrests for the entire composition range between 0 and 100 m/o UF_6 were determined. Solid phases were identified by X-ray diffraction analysis. The phase diagram presented in ANL-7055, p. 132 was revised in accordance with the additional data obtained.

a. EXPERIMENTAL

(1) Materials

The UF_6 used in this work was a portion of a larger batch originally obtained from Oak Ridge National Laboratory. Almost two-thirds of the original batch had been distilled away in previous experimental work, contributing to the purification of the remaining UF_6 from low-boiling impurities (e.g., HF , CF_4 , F_2). Emission-spectrographic analysis of the material indicated that the predominant impurities were P, <400 ppm, and As, B, Cs, Pd, Re, Sb, Sn, and Th, each present at concentrations of <100 ppm. Two determinations of the triple point of a sample of the UF_6 yielded values of 64.1°C and 64.2°C. The best literature value²⁹ for the triple point of UF_6 is 64.05°C.

The MoF_6 was a high-purity material obtained commercially.³⁰ Analysis of the material by emission spectrography indicated that the concentrations of the predominant impurities were P, <20 ppm; Cs, Re, and Sb, <10 ppm; U, <5 ppm; Sn, W, and Zn, <4 ppm; all other impurities were <2 ppm. The triple point of the material was $17.4 \pm 0.5^\circ\text{C}$. Literature values for the triple point are 17.4°C,³¹ 17.5°C,³² and 17.57°C.³³

²⁹ B. Weinstock, E. E. Weaver, and J. G. Malm, Vapor Pressures of NpF_6 and PuF_6 ; Thermodynamic Calculations with UF_6 , NpF_6 , and PuF_6 , J. Inorg. Nucl. Chem. **11**, 104 (1959).

³⁰ A. D. Mackay, Inc., New York, material prepared by General Chemical Division of Allied Chemical Co., Baton Rouge, La.

³¹ G. H. Cady and G. B. Hargraves, The Vapor Pressures of Some Heavy Transition-Metal Hexafluorides, J. Chem. Soc., 1563 (1961).

³² A. P. Brady, O. E. Meyers, and J. K. Clauss, Thermodynamic Properties of Higher Fluorides. I. The Heat Capacity, Entropy, and Heats of Transition of Molybdenum Hexafluoride and Niobium Pentafluoride, J. Phys. Chem. **64**, 588 (1960).

³³ D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, Heat Capacity and Other Thermodynamic Properties of MoF_6 Between 4 and 350°K, J. Chem. Phys. **44**, 2802 (1966).

(2) Containment of Materials

All experimental work with hexafluorides employed a metal manifold constructed of nickel tubing and fittings. The manifold incorporated Monel diaphragm valves³⁴ and a number of 1-in. dia. valves³⁵ with brass bodies, Monel bellows, and Teflon seats. The transfer of hexafluorides from one vessel to another in the manifold was carried out by vacuum distillation at room temperature.

(3) Thermal Analysis Apparatus and Procedure

The apparatus and procedures used in thermal analysis were the same as those described previously (ANL-7055, pp. 127-130). A mixture contained in a nickel sample tube was subjected to thermal analysis. During a run, the tube was positioned in a cavity in a cylindrical nickel block which was heated or cooled. Sample temperatures were measured by a sheathed iron-Constantan thermocouple placed in a well in the bottom of the sample tube.

(4) X-ray Diffraction Procedures

To obtain X-ray diffraction patterns for the hexafluorides, samples were sealed into quartz capillary tubes having a 0.15 to 0.25-mm ID and wall thicknesses of 0.02 to 0.05 mm. The large end (9-mm OD) of each capillary was attached to the nickel vacuum manifold by a vacuum coupling using a neoprene O-ring coated with a grease³⁶ that is resistant to fluorinating agents. After the manifold and capillary tubing were evacuated to a pressure of 3×10^{-4} torr, the capillary was baked using either a heat gun or a brush flame. The hexafluoride was transferred by vacuum distillation at room temperature through the vacuum line, and was condensed into the tip of the capillary. With the bottom of the capillary immersed in liquid nitrogen, the top of the capillary was sealed off with an oxy-gas torch.

The capillaries were positioned in a 114.6-mm Debye-Scherrer camera, and X-ray diffraction photographs were obtained using filtered radiation from $\text{CuK}\alpha$ and $\text{CoK}\alpha$ sources. Subambient temperatures were maintained in the camera by providing a flow of cooled nitrogen within the camera. Both the camera and nitrogen gas lines were insulated with a 1-in. thick covering of Armaflex³⁷ foam.

(5) Determination of Solid Density of the High-Temperature Form of MoF_6

The density of solid MoF_6 at a temperature above its transformation point was determined from measurements of the volume and weight of a small sample. A calibrated quartz tube (9-mm OD) was joined by a brass vacuum coupling to a valve and flare fitting so that it could be attached to the vacuum line.

After a sample of MoF_6 was condensed into the tube, the tube was removed from the vacuum line and weighed to obtain the weight of the MoF_6 by difference. The tube was then clamped in an upright position, and the MoF_6 was solidified by immersing the tube slowly in an ice bath to preclude void formation in the solid. After the MoF_6 completely solidified, the tube was immersed in a constant-temperature water bath, and the height of the solid surface was measured with a cathetometer. The volume of the solid MoF_6 in the calibrated tube was then determined.

b. RESULTS

(1) Thermal Analysis

Although cooling curves (employed in previous work) indicated liquidus points and solid-state transformations, supercooling of the liquids obscured the indication of all solidus points. Many of the thermal analyses were carried out by obtaining heating curves to determine both liquidus points and solidus points. The liquidus data obtained by heating agreed satisfactorily with those obtained from cooling curves.

Table II-15 lists the temperatures of thermal arrests for the entire range of compositions between 0 and 100 m/o UF_6 . The values listed in Table II-15 are averages of replicate measurements, and the uncertainty values are standard deviations of the averages. Several liquidus points obtained from cooling curves are extrapolated values³⁸ and the uncertainties associated with them have not been estimated.

The temperatures of thermal arrests are plotted as a function of composition in Figure II-15. Lines have been drawn to suggest the location of equilibrium phase boundaries and the best interpretation of the thermal analysis data. The resulting diagram is characteristic of a system exhibiting solid solubility with a minimum melting point and a solid miscibility gap.

Changes in the composition of the condensed phases caused by differential vaporization of UF_6 and MoF_6 were estimated. The location of points on the liquidus curve in UF_6 -rich mixtures would be affected more than any others by composition changes, but the com-

³⁴ Valves No. 411 and 413, Hoke Incorporated, One Tenakillark, Cresskill, N. J.

³⁵ Vactronic Lab. Equipment, Inc., East Northport, Long Island, N. Y.

³⁶ Kel-F No. 90 Grease, Minnesota Mining and Mfg. Co., St. Paul, Minn.

³⁷ Armstrong Cork Company, Lancaster, Pa.

³⁸ D. H. Andrews, G. T. Kohman, and J. Johnston, Solubility Relations of Isomeric Organic Compounds, II. The Determination of Freezing Temperatures of Binary Mixtures, *J. Phys. Chem.* **29**, 914 (1925).

TABLE II-15. TEMPERATURES OF THERMAL ARRESTS IN MoF_6 - UF_6 MIXTURES

Mole Fraction UF_6	Liquidus		Solidus		Solid Transition		Solid Transition	
	Cooling (°C)	Heating (°C)	Heating (°C)	Cooling (°C)	Cooling (°C)	Heating (°C)	Cooling (°C)	Heating (°C)
0.964		63.2 ± 0.6	58.0 ± 0.1		5.5 ± 2.6 ^a			
0.910		62.4 ± 1.9	49.1 ± 0.6	14.2 ± 0.0 ^a	6.3 ^a		-2.7 ^a	
0.880		59.4 ± 0.6	43.0 ± 5.0					
0.873	60.8 ^b		12.3 ± 0.1	13.2 ± 0.2 ^a				
0.853		60.4 ± 2.4	43.0 ± 3.3	14.3 ± 0.1 ^a	2.5 ± 0.4 ^a		-3.6 ± 0.3 ^a	
0.809		55.4 ± 0.4	29.0 ± 4.0	14.4 ± 0.3 ^a	3.6 ± 1.6 ^a		-2.0 ± 0.1 ^a	
0.769		55.5 ± 0.8	26.6 ± 5.5	14.4 ± 0.0	2.4 ± 0.2 ^a		-2.2 ± 0.3 ^a	
0.729	52.1 ^b		12.4	13.8 ± 0.2				
0.719		53.2 ± 2.3	22.7 ± 2.6	14.5 ± 0.1	4.0 ± 1.8 ^a		-2.1 ± 0.4 ^a	
0.599		49.5 ± 2.1	13.5 ± 0.2	14.2 ± 0.2	5.9 ± 0.6 ^a		-5.6 ± 2.1 ^a	
0.583	46.4 ^b			13.7 ± 0.2			-3.3 ± 2.1 ^a	
0.516		46.0 ± 0.7	13.6 ± 0.0	14.2	7.7 ^a		-4.3	-8.3 ^a
0.490	40.0 ^b			13.7 ± 0.2			-2.0 ± 2.1 ^a	
0.451		43.6 ± 1.8	13.7 ± 0.1	14.2 ± 0.2	8.0 ± 0.6 ^a		-3.2 ± 1.9 ^a	-7.9
0.404	31.4 ^b		14.2 ± 0.1	13.9 ± 0.1	7.4 ± 0.8 ^a		-3.5 ± 0.7	-7.0 ± 0.7
0.354		33.3 ± 2.2	13.6	14.2 ± 0.2	8.3 ± 0.3 ^a		-4.1 ± 0.6	-8.3 ± 0.6
0.337	27.0 ± 1.6			13.6 ± 0.6	4.9 ± 0.9 ^a		-5.1 ± 1.4	
0.331	29.2 ^b			13.8 ± 0.2	7.3 ± 0.6 ^a		-4.1 ± 1.7	
0.308	21.3 ± 4.1	23.8 ± 1.3	13.6 ± 0.0	14.5 ± 0.1	7.7 ^a			
0.282	19.3 ± 2.5			14.5 ± 0.2	7.3 ± 0.6 ^a		-3.7	
0.276	21.9 ± 0.4		12.5 ± 0.3	13.9 ± 0.4	5.1 ± 1.0 ^a		-8.0 ± 0.3	-6.8 ± 0.1
0.263	>16.8 ^b	14.2 ± 0.1	13.7 ± 0.1	14.4			-4.8 ± 0.5	-4.9
0.237	16.0 ^b	14.1 ± 0.5	13.6 ± 0.4	14.4 ± 0.1	6.8 ± 2.1 ^a		-5.1	
0.231	16.0 ^b			13.4 ± 0.3	7.9 ^a		-4.9 ± 0.6	
0.200				13.0 ± 0.5	9.7 ± 0.7		-2.3 ± 1.5	
0.198		14.2 ± 0.4	13.0 ± 0.6		7.5 ± 3.0			
0.173		14.8 ± 0.4	13.4 ± 0.1		6.0 ± 1.6			
0.166		14.8 ± 0.4	13.2 ± 0.4		4.7 ± 0.7			
0.152		15.2 ± 0.0	13.8 ± 0.0		3.4 ± 0.4	5.1 ± 0.3	-3.1 ± 0.6	-7.6 ± 0.1
0.146					5.8 ± 1.3		-3.2 ± 1.2	
0.116		15.7	14.5		-0.5 ± 0.3	-2.1	-5.7 ± 0.6	-5.5
0.109		15.6 ± 0.0	14.7 ± 0.1		-1.9 ± 0.0	-0.5 ± 1.4	-6.3 ± 0.3	-6.6 ± 0.4
0.0972					-2.5 ± 0.0		-6.1	
0.0702		16.7 ± 0.3	14.7 ± 0.5				-6.2 ± 0.4	-6.9
0.0661		16.8 ± 0.3	15.8 ± 0.2			-0.6 ± 0.4	-6.2 ± 0.1	-7.6 ± 0.4
0.0554		17.2	16.0				-7.4 ± 0.2	-8.5
0.0551		16.6 ± 0.6	15.7 ± 0.4				-6.7 ± 0.0	-8.1
0.0527		17.6 ± 0.5	16.1 ± 0.1				-7.0 ± 2.3	-7.3 ± 0.6
0.0326		17.1 ± 0.2	16.4 ± 0.2				-8.8 ± 0.2	-7.9 ± 0.2
0.0296		17.7	16.2				-9.0 ± 0.2	
0.0							-10.8 ± 0.1	-9.8 ± 0.05

^a Indicates small thermal arrest.^b Values obtained by extrapolation.

positions differed from the mole fraction values calculated from the total weights of the components by less than 1%. Since changes of this size are small compared with the uncertainty of the liquidus curve location in this region, the effects of vaporization on the composition were considered unimportant in constructing the phase diagram from the thermal analysis data.

(2) X-ray Diffraction Analysis

The technique of X-ray diffraction analysis has been used to determine the crystal structure change associated with the variable thermal halt (ANL-7055,

p. 134) between 0 and 0.23 mole fraction UF_6 . The crystal structures for pure MoF_6 and for MoF_6 - UF_6 mixtures were determined in two particular areas of the diagram. The crystal structures of pure MoF_6 below -9°C and also between -9°C and $+17.4^\circ\text{C}$ were studied since thermal analysis had shown that solid-state transformation of pure MoF_6 occurred at $-10.8 \pm 0.1^\circ\text{C}$ (from cooling curves) or $-9.8 \pm 0.05^\circ\text{C}$ (from heating curves).

X-ray diffraction powder photographs of MoF_6 taken at $+10^\circ\text{C}$ can be indexed on the basis of a body-centered cubic unit cell with a lattice constant, $a =$

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FIG. II-15. Phase Equilibria in the Condensed System UF_6 - MoF_6 .

$6.23 \pm 0.01 \text{ \AA}$. The similarity of the MoF_6 diffraction pattern to that of molybdenum metal indicates that the molybdenum atoms in the hexafluoride, as in the metal, are located at the body center and corners of a cube.

X-ray diffraction powder photographs taken below -9°C are indexable on the basis of an orthorhombic unit cell. Lattice constants from a pattern obtained at -20°C are $a = 9.65 \pm 0.02 \text{ \AA}$, $b = 8.68 \pm 0.03 \text{ \AA}$, and $c = 5.05 \pm 0.02 \text{ \AA}$. An orthorhombic MoF_6 diffraction pattern was therefore calculated using these lattice constants and the atomic coordinates derived by Hoard and Stroupe for UF_6 .³⁹ The agreement between calculated and observed values for MoF_6 listed in Table II-16 indicates that the low-temperature structure of MoF_6 is similar to, but not necessarily identical to, the orthorhombic structure of UF_6 .

The crystal structure change associated with the solid-state transformation of pure MoF_6 , i.e., body-centered cubic above the transformation temperature to orthorhombic below it, is analogous to the cubic-to-orthorhombic transformation reported⁴⁰ for the 5d hexafluorides, WF_6 , ReF_6 , OsF_6 , IrF_6 , and PtF_6 .

The X-ray diffraction patterns of UF_6 - MoF_6 mixtures at UF_6 -rich and MoF_6 -rich compositions were studied to determine any effect of the minor constituent on crystal lattices. X-ray diffraction patterns

³⁹ J. L. Hoard and J. D. Stroupe, in *Chemistry of Uranium*, collected Papers, J. J. Katz, Ed., TID-5290, Book 1, p. 325, 1958.

⁴⁰ B. Weinstock, *Rotation and Molecular Distortion in the Condensed Phases of Hexafluoride Molecules*, J. Phys. Chem. Solids **18**, 86 (1961).

obtained from mixtures with 5 m/o UF_6 at 6°C and 14 m/o UF_6 at 0 to 7°C appeared to be the same as patterns obtained from the high-temperature form of pure MoF_6 . X-ray diffraction patterns obtained from a mixture with 91 m/o UF_6 at 0 to 5°C appeared to be the same as a pattern obtained for pure UF_6 .

(3) Density of High-Temperature Solid MoF_6

The density of solid MoF_6 was obtained from weight and volume measurements at two temperatures above its transformation point. At $+8^\circ\text{C}$, the density was 2.91 g/cc , and at 0°C , the density was 2.88 g/cc . The density calculated from X-ray diffraction data obtained on pure MoF_6 at $+10^\circ\text{C}$ on the basis of a body-centered cubic unit cell containing 14 atoms ($2 \times \text{MoF}_6$) was 2.88 g/cc . The agreement between the value calculated from X-ray diffraction data and that obtained from weight and volume measurements appears to confirm the cubic structure for the high-temperature form of pure MoF_6 .

c. DISCUSSION

(1) Nonequilibrium Thermal Arrests

Those points in Figure II-15 not representing phase boundaries may be explained in terms of nonequilibrium cooling or heating. A number of small thermal arrests are located in the region labelled S_2 in the diagram (Figure II-15) where, according to the interpretation given below, only the primary solid solution S_2 is stable. These thermal arrests are attributed to fractional crystallization which occurs if diffusion

TABLE II-16. POWDER DIFFRACTION DATA^a FOR LOW-TEMPERATURE (ORTHORHOMBIC) FORM OF MoF_6

<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	<i>I</i> _{obs} ^b	<i>I</i> _{calc}
101	4.48	4.47	W	38
011	4.36	4.36	W	24
020		4.34		57
210	4.19	4.22	S	100
111	3.98	3.98	M	66
201	3.48	3.49	W	16
121	3.11	3.11	F	29
221	2.708	2.719	M	11
301		2.713		13
311	2.580	2.589	F	14
230	2.473	2.481	F	18
112	2.349	2.351	F	12
321	2.298	2.300	F	14
202	2.234	2.237	W	12
231		2.227		23

^a Obtained with cobalt $K\alpha$ radiation.

^b S = strong, M = medium, W = weak, F = faint.

in the solid phase is not fast enough to allow the establishment of equilibrium between solid and liquid phases during crystallization.⁴¹ In the extreme case of no solid state diffusion, the first nucleus (or nuclei) of solid formed when the mixture is cooled is completely removed from the reaction. As cooling proceeds, the crystal nucleus becomes the core of a layered structure, each succeeding layer being poorer in the higher-melting component (UF_6). With the removal of UF_6 -rich liquid from the reaction, the composition of the remaining liquid proceeds along the liquidus curve and approaches the composition of the minimum-freezing mixture as a limit, while the freezing point of the remaining liquid approaches the eutectic point as a limit. Thus, for a mixture with a total composition of 80 or 90 m/o UF_6 , the last-remaining portion of liquid to freeze may have the composition of the eutectic mixture (~ 22 m/o UF_6).

In this work, no annealing of the solid phase was done. In this case, when the mixture is heated to obtain a melting curve, the first of the solid to melt will be the outer layer with the composition and melting point of the eutectic mixture. Thus, on heating UF_6 -rich mixtures, the first slight absorption of thermal energy at constant temperature was observed at the eutectic point, but the major and definite thermal arrests occurred at higher temperatures; these latter points were assumed to indicate the location of the solidus curve.

Very small heat effects yielding thermal arrests at $+5^\circ\text{C}$ have been observed over a wide range of composition. These heat effects are so small as to be observed only by differential thermal analysis at high amplification of the thermocouple signal. All other arrests were easily observed at rates of $0.6^\circ\text{C}/\text{min}$, whereas the effects at $+5^\circ\text{C}$ were observed only for faster cooling rates (3 to $6^\circ\text{C}/\text{min}$), suggesting a nonequilibrium situation. The arrests at $+5^\circ\text{C}$ are interpreted as the result of a combination of fractional crystallization and supercooling of the liquid of eutectic composition. In nonequilibrium cooling of any mixture on the UF_6 -rich side of the eutectic, the composition of the last-remaining portions of liquid would decrease in UF_6 until the eutectic point is reached. The composition of mixtures which supercool below the eutectic temperature follows an extension of the liquidus curve.⁴² Thus, a small, last-remaining portion of liquid could cool below the eutectic temperature to about 5°C , at which point the composition of the

liquid becomes equal to the composition at the boundary of the solid state miscibility gap, and upon freezing of the liquid, a small heat effect is generated.

(2) The Effect of UF_6 on the MoF_6 Solid-State Transformation

The temperature of the solid-state transformation of pure MoF_6 obtained by thermal analysis is $-10.8 \pm 0.1^\circ\text{C}$ from cooling curves and $-9.8 \pm 0.05^\circ\text{C}$ from heating curves. Literature values for this solid-state transformation are -8.7°C , obtained from the intersection of vapor pressure curves;³¹ -9.6°C , obtained in a calorimetric study;³² and -9.68°C , also obtained in a calorimetric study.³³

The results of thermal analysis show that the temperature of the solid-state transformation in MoF_6 - UF_6 mixtures is approximately -5°C rather than approximately -10°C as in pure MoF_6 . This behavior creates a peritectoid on the MoF_6 -rich side of the diagram in Figure II-15. If the solid-state transformation temperature of a component A increases when another component B is added, this indicates that component B is more soluble in the low-temperature form of component A than in the high-temperature form of component A.⁴¹ It is therefore concluded, on the basis of the observed increase in the transformation temperature (not on the basis of a chemical analysis of solids S_1 and S_3), that UF_6 is more soluble in the low-temperature form of MoF_6 than in the high-temperature form.

This conclusion might be anticipated on the basis of the crystal structures: A solid of orthorhombic structure (UF_6) is expected to be more soluble in another solid of orthorhombic structure (low-temperature form of MoF_6) than in a solid of cubic structure (high-temperature form of MoF_6).

(3) Comparison of Solid Solubilities

The limit of solid miscibility has been related to the energy of distortion of the crystal lattice when atoms of a second component are introduced into the lattice; Hildebrand and Scott⁴³ and Lawson⁴⁴ have expressed the distortion energy as a function of the molal volumes of the two components. These authors recognized that the solubility of small atoms in a lattice of large atoms is greater than the solubility of large atoms in a lattice of small ones. The same relationship presumably holds for molecular lattices. The solid-solubility relations indicated in Figure II-15

⁴¹ J. E. Ricci, Guide to the Phase Diagrams of the Fluoride Systems, ORNL-2396, p. 5, December 1958.

⁴² W. Hume-Rothery, J. W. Christian, and W. B. Pearson, *Metallurgical Equilibrium Diagrams*, The Institute of Physics, London, 1952, p. 34.

⁴³ J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Ed., Reinhold Publishing Corp., New York 1950, p. 304.

⁴⁴ A. W. Lawson, On Simple Binary Solid Solutions *J. Chem. Phys.* **15**, 831 (1947).

are in accord with this thesis. The molal volumes⁴⁵ are 84 cm³ for MoF₆ and 96 cm³ for UF₆. Figure II-15 indicates that the maximum solubility (~30 m/o MoF₆) of the smaller MoF₆ molecule in the primary solid solution S₂ (presumably the UF₆ lattice) is greater than the maximum solubility (~12 to 18 m/o UF₆) of the larger UF₆ molecule in either of the primary solid solutions, S₁ or S₃ (presumably MoF₆ lattices).

(4) Correlation of X-ray Diffraction Patterns from MoF₆-UF₆ Mixtures with the Phase Diagram

X-ray diffraction patterns from mixtures with 5 m/o

UF₆-95 m/o MoF₆ at 6°C and 14 m/o UF₆-86 m/o MoF₆ at 0 to 7°C appeared to be the same as those obtained from the high-temperature form of pure MoF₆, suggesting a cubic structure. According to Figure II-15, the stable phase in these mixtures is the primary solid solution S₁ which would be expected to have the lattice of the high-temperature form of pure MoF₆.

The X-ray diffraction pattern from a mixture of 9 m/o MoF₆-91 m/o UF₆ at 0 to 5°C appeared to be the same as that obtained for pure UF₆. Figure II-15 shows that the stable phase in this mixture is the primary solid solution S₂, which would be expected to have the lattice of pure UF₆.

5. The Melting-Point Diagram of the System UF₆-PuF₆ (L. TREVORROW, D. STEIDL)

a. INTRODUCTION

Certain unit operations considered for fluoride volatility processes involve mixtures of UF₆ and PuF₆ in the condensed state. A thorough understanding of the behavior of these mixtures is necessary for the design of process equipment for handling the condensed hexafluorides. Therefore, experimental determinations of the melting points of UF₆-PuF₆ mixtures were made to provide information on the solid-liquid equilibria and to construct a temperature-composition diagram.

b. EXPERIMENTAL DETAILS

(1) Containment of Materials

The hexafluorides were contained in the type of equipment used in work with the MoF₆-UF₆ system as described above. The equipment and the glovebox in which it was housed are described in an earlier report (ANL-6925, pp. 120-122).

(2) Materials

The UF₆ used in this work was taken from the same batch as that described above in the study of the MoF₆-UF₆ system.

The PuF₆ was prepared in this laboratory by reaction of fluorine with PuF₄ at 550°C. The PuF₄ contained Ca (<25 ppm), Fe (<20 ppm), and Sb (<20 ppm) as predominant impurities. After preparation, the PuF₆ was freed from low-boiling impurities by a technique similar to that described by Weinstock and Malm.⁴⁶ Two determinations of the triple point of a

sample of purified PuF₆ yielded values of 51.5 and 51.3°C. The best literature value²⁹ for the triple point of pure PuF₆ is 51.59°C.

(3) Thermal Analysis Apparatus and Procedure

The apparatus and procedure used for thermal analysis were the same as those used in the study of the MoF₆-UF₆ system (ANL-7055, p. 127).

After 1 to 4 g of PuF₆-UF₆ had been loaded into the sample tube, the tube was heated to 70°C to melt both components and then agitated to mix the components. The tube was then placed against a block of dry ice to condense the hexafluorides into the bottom of the tube.

For each sample mixture, approximate values of the thermal arrests were obtained by rapidly heating or cooling the sample. The mixture was then heated at a programmed rate to obtain accurate values of the thermal arrests from which solidus and liquidus temperatures were determined. After the sample had melted, it was cooled, and the procedure was repeated for several determinations of the melting point.

Upon completion of the thermal analysis, the hexafluoride mixture was distilled into a waste trap filled with activated alumina. The sample tube was then detached from the valve assembly, and any solids remaining in the tube were removed. In some runs, the hexafluoride mixture remained in the tube for several days, and a quantity of fluffy solid (presumably PuF₄ formed by radiation decomposition of PuF₆) accumulated in the tube. The sample tube was then conditioned with fluorine before reuse.

c. RESULTS

Figure II-16 shows examples of records of the voltages of both the sample thermocouple and the differ-

⁴⁵ J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Ed., Reinhold Publishing Corp., New York, 1950, p. 436.

⁴⁶ B. Weinstock and J. G. Malm, *The Properties of Plutonium Hexafluoride*, J. Inorg. Nucl. Chem. **2**, 380 (1956).

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FIG. II-16. Thermocouple Voltages during Melting of a $\text{UF}_6\text{-PuF}_6$ Mixture (45.8 m/o UF_6). Heating rate: 0.3°C/min

ential thermocouple obtained during the melting of a mixture of $\text{UF}_6\text{-PuF}_6$ (45.8 m/o UF_6). The shape of the record (melting curve) indicates that melting takes place over a range of temperatures. All mixtures yielded similar melting curves. The solidus and liquidus points were determined by intersections of the extensions of linear portions of the curves as suggested by Findlay.⁴⁷ Although the liquidus and solidus points could be derived accurately from some sample thermocouple curves such as that in Figure II-16, in some cases the differential thermocouple curve was necessary for these determinations since the sample thermocouple curve did not show the solidus and liquidus clearly.

Utilization of cooling curves for the measurement of liquidus and solidus points was evaluated. Liquidus points could not be determined accurately from cooling curves because of supercooling effects. A typical mixture supercooled extensively, and then crystallized suddenly. The heat-transfer characteristics of the

sample block assembly were such that the heat released in freezing of the small samples was insufficient to raise the sample temperature enough to yield an accurate determination of the liquidus point from cooling curves even by an extrapolation procedure. Neither manual bumping nor mechanical vibration was effective in eliminating supercooling of the $\text{UF}_6\text{-PuF}_6$ samples. Small samples (1 to 4 g) were used in the present work to maintain homogeneity in the absence of stirring, and to avoid the frequent preparation of PuF_6 . The maximum temperature usually attained by the $\text{UF}_6\text{-PuF}_6$ mixtures upon crystallization after supercooling was the solidus point. The sharp maximum on the temperature record, however, did not appear to be a reliable measure of the solidus point. All data for the measurement of the solidus and liquidus points were obtained from records of melting determinations. Table II-17 lists the solidus and liquidus temperatures for the entire range of compositions between 0 and 100 m/o UF_6 . Two to five melting curves were obtained for each mixture. Values for liquidus and solidus temperatures listed in Table II-17 are average and the uncertainty values are standard deviations from the averages.

⁴⁷ A. Findlay, *The Phase Rule and Its Applications*, Longmans, Green and Company, Inc., New York, 1938, pp. 474-476 (also published by Dover Publications, New York).

TABLE II-17. TEMPERATURES OF THERMAL ARRESTS IN UF_6 - PuF_6 MIXTURES

Uncorrected Mole Fraction ^a UF_6	Liquidus Point ^b (°C)	Solidus Point ^b (°C)	Correction of Mole Fraction UF_6 for Differential Volatilization of PuF_6 and UF_6		Maximum Correction ^c of Mole Fraction UF_6 for Radiation Decomposition
			At liquidus	At solidus	
0.0506	53.0 ± 0.1	51.6 ± 0.1	-0.002	0.000	
0.132	53.6 ± 0.2	51.5 ± 0.4	-0.001	0.000	+0.002
0.141	53.6 ± 0.1	52.8 ± 0.1	-0.000	0.000	
0.220	54.0 ± 0.1	53.2 ± 0.2	-0.002	-0.001	
0.244	54.2 ± 0.3	52.8 ± 0.1	-0.002	0.000	+0.004
0.307	55.6 ± 0.3	54.3 ± 0.0	-0.001	0.000	
0.323	54.7 ± 0.2	53.8 ± 0.1	-0.005	-0.001	+0.004
0.388	57.0 ± 0.8	54.7 ± 0.3	-0.003	0.000	+0.005
0.458	56.9 ± 0.1	56.1 ± 0.2	-0.001	0.000	
0.501	57.8 ± 0.1	56.1 ± 0.2	-0.002	-0.001	
0.503	57.5 ± 0.4	55.8 ± 0.4	-0.004	-0.001	
0.581	59.4 ± 0.9	57.1 ± 0.6	-0.002	-0.001	
0.677	60.3 ± 0.5	58.7 ± 0.4	-0.003	0.000	+0.005
0.684	59.6 ± 0.1	58.3 ± 0.2	-0.003	-0.001	+0.005
0.714	60.9 ± 0.3	59.1 ± 0.2	-0.002	0.000	+0.004
0.751	60.9 ± 0.1	59.5 ± 0.3	-0.002	0.000	+0.004
0.851	62.4 ± 0.3	61.3 ± 0.0	-0.001	-0.001	
0.876	62.8 ± 0.1	61.8 ± 0.1	-0.001	-0.001	
0.924	63.6 ± 0.1	61.9 ± 0.1	0.001	0.000	+0.001
0.946	64.4 ± 0.4	62.5 ± 0.3	0.000	0.000	+0.001
0.964	64.0 ± 0.1	63.5 ± 0.0	0.000	0.000	

^a Mole fractions calculated from total weights of components.

^b Listed values are each averages of two to five determinations. The uncertainties are standard deviations of the averages.

^c Maximum correction, calculated by assuming that all alpha energy is absorbed by PuF_6 to give PuF_4 and that any UF_4 formed would be refluorinated to UF_6 by PuF_6 .

d. DISCUSSION

(1) Melting-Point Diagram

The plot of the solidus and liquidus temperatures as a function of composition in Figure II-17 shows a diagram characteristic of a continuous series of solid solutions. The stable phases are liquid, liquid in equilibrium with solid solution, and solid solution.

A mixture with a composition of 50.3 m/o UF_6 was cooled to -9°C to determine if any thermal arrests would be observed at temperatures below the solidus point, indicating a miscibility gap in the solid solution. No thermal arrests were observed between the solidus point and -9°C . The result of this cursory search, however, is not incontrovertible evidence that a miscibility gap does not exist. Even if the equilibrium state of a given solid system involves two phases, this may remain undetected by thermal analysis if the process of changing to a two-phase system involves diffusion in the solid state and is slow.⁴⁸

⁴⁸ J. C. Wooley and B. A. Smith, *Solid Solutions in A^{III}B^V Compounds*, Proc. Phys. Soc. (London) **72**, 214 (1958).

(2) Factors Influencing Solid Miscibility of UF_6 - PuF_6 System

The major physical attributes of pure components affecting phase equilibria in binary mixtures are those properties which determine solid miscibility:⁴⁹ heat of mixing, distortion energy, and crystal structure compatibility. Each of these properties was examined in order to predict the solid-phase behavior in the UF_6 - PuF_6 system and compare the behavior to the experimental observation of complete solid miscibility. It was found that none of these properties affects the phase equilibria in this system and therefore the condensed phase equilibria in the UF_6 - PuF_6 system would be expected to be a continuous series of solid solutions.

(3) Comparison of Observed Behavior with Ideal Behavior

The curves in Figure II-17 representing the locus of ideal solidus and liquidus temperatures were calcu-

⁴⁹ J. H. Hildebrand and R. L. Scott, *The Solubility of Non-electrolytes*, 3rd Ed., Reinhold Publishing Corp., New York, 1950, pp. 300-319.

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FIG. II-17. Melting-Point Diagram for the System UF_6 - PuF_6 .

lated from equations derived on the assumption that Raoult's law holds for both the liquid solutions and for the solid solutions.⁵⁰

In an isoplethal comparison (i.e., at the same composition), all of the observed solidus temperatures lie below the ideal values; the average difference of observed solidus temperatures from the ideal curve is -1.0°C . In an isothermal comparison, the observed equilibrium compositions contain more UF_6 than suggested by the ideal system; the average difference of observed compositions from the ideal values is $+8.0$ m/o UF_6 .

The deviation of observed liquidus points from the ideal is somewhat less than the deviation of observed solidus points from the ideal. On an isoplethal basis, the average positive and negative deviations of observed liquidus values from ideal liquidus values are $+0.3^\circ\text{C}$ and -0.7°C . On an isothermal basis, the average deviations, as observed from ideal liquidus values, are $+4.6$ m/o UF_6 and -2.1 m/o UF_6 .

While the observed liquidus points are scattered in the vicinity of the ideal liquidus curve, the observed solidus points all lie below the ideal solidus curve.

⁵⁰ H. Seltz, Thermodynamics of Solid Solutions. I. Perfect Solutions, J. Am. Chem. Soc. 56, 307 (1934).

Two possible causes of the bias of observed solidus points with respect to the ideal solidus curve were considered: soluble impurities and fractional crystallization. The contribution of each of these points to non-ideal behavior in phase equilibria determinations was discussed in Section II A 4 in regard to the UF_6 - MoF_6 system, and the conclusions stated there are pertinent to the UF_6 - PuF_6 system.

The presence of a soluble impurity in the system, such as HF , is not a satisfactory explanation for the observed behavior, since the presence of the impurity would result in the lowering of the melting points of the pure components and such effects were not observed.

Long annealing times were not feasible for the UF_6 - PuF_6 system owing to the formation of relatively large amounts of PuF_4 by the radiation decomposition of PuF_6 . The effects of PuF_4 on the temperature measurements could not be clearly defined. No annealing of the solid was performed prior to thermal analysis measurements. The establishment of equilibrium between liquid and solid phases by an extremely low rate of cooling during freezing, prior to a melting point determination, was not possible owing to supercooling effects.

Corrosion of Nickel and Nickel-containing Alloys by Fluorine and Volatile Fluorides (W. H. GUNTHER, M. J. STEINDLER)

a. INTRODUCTION

The fluoride volatility program is designed to develop nonaqueous processes for the recovery of uranium and plutonium from partially spent nuclear reactor fuels by the formation of the volatile hexafluorides of uranium and plutonium, which are subsequently separated from the volatile fission product fluorides. Nickel or nickel alloys such as Monel are commonly used as the material of construction for process equipment which is to be exposed to fluorine and to corrosive fluorides at elevated temperatures, since extensive attack on these materials is generally prevented by the formation of a protective nickel fluoride scale which limits further reaction. In order to make estimates of the expected useful lifetimes of such equipment exposed to fluorine, UF_6 , PuF_6 , and the volatile fission product fluorides at temperatures up to $550^\circ C$, a knowledge of corrosion rates by these fluorides is required.

The series of small-scale corrosion experiments reported in ANL-7125, pp. 79-85, have been continued. In recent experiments, performed at $500^\circ C$, nickel-200, nickel-201, Monel, Inconel, Duranickel alloy 301, HyMu-80, and INOR-8 coupons have been exposed to fluorine and UF_6 and to some of the following fission product fluorides individually and in the presence of fluorine: GeF_4 , AsF_5 , TeF_6 , SeF_6 , MoF_6 , BrF_5 , NbF_5 , and SbF_5 . In several experiments, coupons containing areas of nickel-200 weld, nickel-61 weld, and cadmium-free silver solder were used. Corrosion rates were calculated from the weight change of the coupons after reaction. Intergranular penetration of the base metal was observed in many of the coupons. The nominal chemical composition for all of the metals used in this study are tabulated in Table II-18.

b. CORROSION BY FLUORINE, UF_6 , AND FISSION PRODUCT FLUORIDES

(1) Experimental

A description of the corrosion apparatus and experimental procedure has been presented previously in ANL-7125, pp. 79-80. The procedure was to expose coupons to fluorine, a corrosive fluoride, or a mixture of fluorine and a corrosive fluoride in a heated nickel reaction vessel for a predetermined time at $500^\circ C$.

The coupons were used as received after an initial degreasing step. Most of the fission product fluorides were purified by vacuum distillation and the purity of the fluorides was ascertained by measurements of vapor pressure and vapor density, and by chemical and infrared spectral analyses. The fluorine was passed through an NaF trap heated to $100^\circ C$ to remove trace quantities of HF prior to use.

The specimen coupons were approximately 1 by 1.5 cm and ranged in thickness from 0.15 to 0.34 cm. The coupons, which had small holes drilled in each end, were weighed and connected together by nickel wire. After ten coupons were connected, the top coupon was fastened to a hook welded onto a $\frac{3}{4}$ -in. male flare fitting and the reaction vessel was sealed to the flare fitting with a copper gasket.

The reactant gases were added to the vessel at room temperature except for fluorides of low volatility (NbF_5 and SbF_5), for which the reaction vessel and all lines including the Booth-Cromer pressure transmitter were heated to about $180^\circ C$ to prevent condensation prior to the admission of the gases. The storage vessels containing NbF_5 or SbF_5 were attached to the reaction vessel and were heated to temperatures necessary to maintain a pressure of about 100 mm Hg. The pressure of fluorine was maintained at 575 ± 100 mm

TABLE II-18. NOMINAL CHEMICAL COMPOSITIONS OF NICKEL AND NICKEL ALLOYS
(weight percent)

Alloy	Ni	C	Mn	Fe	S	Si	Cu	Cr	Ti	Al	Mo	Co
Nickel-200	99.5	0.06	0.25	0.15	0.005	0.05	0.05	—	—	—	—	—
Nickel-201	99.5	0.01	0.20	0.15	0.005	0.05	0.05	—	—	—	—	—
Monel	65.0	0.15	0.60	1.00	0.005	0.15	29.5	—	0.50	2.80	—	—
Inconel	76.0	0.04	0.20	7.20	0.007	0.20	0.10	15.8	—	—	—	—
HyMu-80	79.0	0.05	0.50	16.00	—	0.15	—	—	—	—	4	—
INOR-8	70.0	0.06	0.80	5.00	0.010	0.30	0.35	7.0	—	—	16	0.2
uranickel-301	94.0	0.15	0.25	0.15	0.005	0.55	0.05	—	0.50	4.50	—	—
ickel-61 welding rod	93.0	0.15	1.00	1.00	0.010	0.75	0.25	—	2.0-3.5	1.50	—	—
Nickel-200 welding rod	99.5	0.06	0.25	0.15	0.005	0.05	0.05	—	—	—	—	—

Hg and the pressure of fission product fluorides or UF_6 was maintained at 100 ± 20 mm Hg. When fluorine was not present, a fission product fluoride or UF_6 was periodically added to the reaction vessel when the pressure dropped to 80 mm as a result of consumption of reagents. However, when fluorine was present together with a fission product fluoride, the reaction vessel was evacuated and a fresh mixture was added when required.

At the conclusion of an experiment, the reactor was evacuated and allowed to cool slowly to room temperature. The coupons which did not show appreciable spalling of the fluoride scale were reweighed and corrosion rates were calculated from the weight gain of the coupon, assuming that only NiF_2 had formed on the surface of the coupon. Corrosion rates of some coupons were determined by a second method also, in which coupons were descaled in an equimolar bath of $\text{KNO}_3\text{-NaNO}_3$ for $\frac{1}{2}$ hr at 500°C . This descaling procedure allowed corrosion rates to be calculated from the weight loss of the descaled coupons, assuming complete removal of all corrosion scale. To determine the effect of this salt bath on the metals, fresh coupons of all the metals used in this study were placed in a bath at 500°C for $1\frac{1}{2}$ hr, or three times longer than normal. This longer descaling period resulted in apparent corrosion rates of less than 0.001 mil/hr for all of the metals tested. No significant intergranular penetration was noted in fresh coupons exposed to the descaling bath for $\frac{1}{2}$ hr at 500°C .

The extent of intergranular penetration was determined by microscopic examination of exposed coupons which had been polished and etched. None of the etchants tried brought out a crystal structure of the areas containing silver solder. The following etchants and etching times were used:

Nickel-200, Nickel-201, Nickel-200 weld and Nickel-61 weld. A 1:1 mixture of concentrated nitric acid and glacial acetic acid, for 10 to 60 sec.

Monel. An aqueous solution of 10% NaCN -10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$, for 30 to 60 sec.

Inconel, Duranickel-301, HyMu-80, and INOR-8. An aqua regia solution saturated with CuCl_2 , for 10 to 60 sec.

(2) Results

The results of the corrosion tests of nickel and nickel alloys by fluorine, UF_6 , and some of the volatile fission product fluorides at 500°C are tabulated in Table II-19 as mils of metal reacted per hour of exposure. Rates are calculated both from the weight gain of the coupon after exposure assuming that only NiF_2 was formed, and from the weight loss following immersion of the coupons in an equimolar $\text{KNO}_3\text{-NaNO}_3$ salt

bath assuming complete removal of all scale. Corrosion rates for the areas of silver solder are calculated assuming that only AgF was formed on the silver-soldered surface, and deducting the average corrosion rate of nickel-200 by the corrosive environment.

The results of the microscopic examination are listed in Table II-20 as total penetration in mils.

Neither nickel-200 weld nor nickel-61 weld (not listed in Table II-20) showed any intergranular penetration of the weld itself or at the junction of the weld and the base metal. Intergranular penetration of silver solder could not be determined because of the apparent noncrystalline structure of the solder.

Fluorine. Most of the alloys were exposed to fluorine for 6.3 to 26.6 hr at 500°C . The nickel-201 and the welded coupons were only slightly dulled as a result of reaction with fluorine. The welded areas showed no greater corrosion than the nickel-200 portions of the coupons. The Duranickel-301 and HyMu-80 coupons were coated with a green scale whereas the INOR-8 coupons were covered with a very uniform, adherent gold-colored scale. A thin pink scale was formed on the silver-soldered portions of the coupons. The silver-soldered coupons were the most severely corroded. This study revealed no difference in the rates of corrosion of nickel-200 weld and nickel-61 weld by fluorine at 500°C . Both types of weld corroded at a rate of about 0.001 mil/hr. It is interesting to compare our findings with those of Chilenskas and Gunderson⁵¹ for nickel plate welded with nickel-200 and nickel-61 welding rods and exposed to 50 v/o fluorine in nitrogen at 475°C for 240 hr. These exhibited corrosion rates of less than 0.001 mil/hr and 0.150 mil/hr, respectively.

X-ray diffraction analyses of the corrosion scales from all coupons examined showed the presence of only NiF_2 . However, X-ray spectral analyses revealed the following elements to be present in scale removed from coupons: *HyMu-80*: major, nickel; intermediate, iron; very minor, chromium. *INOR-8*: major, nickel; minor, iron, chromium, and manganese; possible minor, molybdenum. *Silver solder*: major, silver, copper, and zinc; minor, nickel and iron.

Germanium Tetrafluoride. When GeF_4 alone was the reactant gas, the coupons were coated with a uniform gray-black scale identified by X-ray diffraction as GeO_2 and NiF_2 . However, when fluorine was present with GeF_4 , the resultant scales were typical of those formed in fluorine.

Arsenic Pentafluoride. In the presence of AsF_5 alone,

⁵¹ A. A. Chilenskas and G. E. Gunderson, Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 7, The Corrosion of Nickel in Process Environments, ANL-6979, March 1965.

nickel-201, both types of nickel weld, Duranickel-301, and INOR-8 coupons showed little evidence of reaction. Dark-colored corrosion scales were present on the HyMu-80 and silver-soldered coupons. The scale from the HyMu-80 coupon was shown to be NiF_2 by X-ray diffraction analysis. When fluorine was present with AsF_5 , the corrosion products were typical of those formed in fluorine.

Tellurium Hexafluoride. When TeF_6 alone was the reactant gas, all of the exposed coupons were quite severely corroded and covered with a gray scale. Spalling of the corrosion scale was evident on most coupons. However, when fluorine was present with TeF_6 , the nickel-200 and Monel coupons showed little evidence of reaction. A similar reduction in rate was not observed with the Inconel, Duranickel-301, HyMu-80, and INOR-8 coupons.

Selenium Hexafluoride. Duranickel-301, HyMu-80, and INOR-8 coupons were exposed to SeF_6 alone and in the presence of fluorine at 500°C for 7.2 and 7.6 hr, respectively. The exposure of all coupons to SeF_6 alone resulted in the formation of a thin black scale with a few areas of white scale present, mainly around the edges of the coupon. When fluorine was present with SeF_6 , the resultant scales were typical of those formed in fluorine.

Molybdenum Hexafluoride. Duranickel-301, HyMu-80, and INOR-8 coupons were exposed to MoF_6 alone and in the presence of fluorine at 500°C for 7.0 and 7.8 hr, respectively. Upon exposure to MoF_6 , a gray scale was formed on the surface of all the coupons. A few of the coupons had areas where a black crystalline solid had formed, which was shown by X-ray diffraction analysis to be probably a rhombohedral form of MoF_3 . When fluorine was present with MoF_6 , the corrosion products were typical of those formed in fluorine.

Bromine Pentafluoride. Nickel-200, Monel, Duranickel-301, and nickel-200 coupons containing areas of nickel-61 weld were exposed to BrF_5 alone and in the presence of fluorine at 500°C for 27.8 and 7.8 hr, respectively. At the end of both experiments the coupons were coated with a dark scale. The scale from a Monel coupon which had been exposed to BrF_5 alone was shown by X-ray diffraction analysis to be NiF_2 as a major phase with possible minor phases of AlF_3 and CuF_2 . X-ray spectral analysis of the same scale showed nickel and copper to be present and bromine and iron to be absent.

Niobium Pentafluoride. Nickel-200, Monel, Duranickel-301, and nickel-200 containing areas of nickel-61 weld were exposed to NbF_5 alone and in the presence of fluorine at 500°C for 21.8 and 5.1 hr, re-

spectively. When NbF_5 alone was the reactant gas, no evidence of reaction was observed. However, when fluorine was present with NbF_5 , the resultant scales were typical of those formed in fluorine.

Antimony Pentafluoride. Nickel-200, Monel, Duranickel-301, and nickel-200 coupons containing areas of nickel-61 weld were exposed to SbF_5 alone and in the presence of fluorine at 500°C for 7.2 and 7.0 hr, respectively. The nickel-200, Monel, and the welded coupons were quite severely corroded by SbF_5 and were uniformly coated with a green and black scale for nickel and a green and violet scale for Monel. X-ray diffraction analyses indicated only NiF_2 to be present in the green scale from the nickel-200 coupon, and NiF_2 plus an unidentified minor phase to be present in the violet scale from the Monel coupon. X-ray spectral analysis of the violet scale showed nickel to be the major element with copper present in smaller amounts. No antimony was detected in the violet scale. The Duranickel-301 coupons exposed to SbF_5 were the least corroded and were uniformly covered with a dark scale. When fluorine was present with SbF_5 , all coupons were generally coated with a green scale. The welded portions of the coupons containing areas of nickel-61 weld were very severely corroded as evidenced by a lateral outgrowth of scale. Examination of the welds after descaling revealed that some areas had up to a total of twenty mils of weld reacted during the experiment.

Uranium Hexafluoride. All of the alloys were exposed to UF_6 individually and in the presence of fluorine at 500°C for 7.0 to 7.6 hr. In general, when the coupons were exposed to UF_6 alone, the corrosion was localized with large areas of scale adjacent to relatively unreacted areas. The silver-soldered portions of the coupons were uniformly covered with a green scale. When fluorine was present with UF_6 , the corrosion of the coupons was much more uniform. All of the coupons were coated with a greenish scale with evidence of local spallation of scale.

(3) Discussion

If the behavior of nickel^{51, 52} is also considered typical for nickel-rich alloys, it can be assumed that rates of corrosion derived from short-term experiments such as these should be considerably greater than rates derived from long-term experiments. For this reason, data such as those listed in Table II-19 represent maximum corrosion rates for the indicated metals. Since the effect of exposure time on the rate of intergranular

⁵² R. L. Jarry, W. H. Gunther, and J. Fischer, The Mechanism and Kinetics of the Reaction between Nickel and Fluorine, ANL-6684, August 1963.

TABLE II-19. CORROSION OF NICKEL AND NICKEL-CONTAINING ALLOYS BY SELECTED VOLATILE FLUORIDES

Temperature: 500 ± 10°C
 UF₆ or F.P. Fluoride Pressure: 100 ± 20 mm
 Fluorine Pressure: 575 ± 100 mm

Experiment Number	Corrosive Environment	Time (hr)	Corrosion Rate ^a (mil/hr)									
			Nickel-200	Nickel-201	Monel	Inconel	Duranickel-301	HyMu-80	INOR-8	Ni-200 Weld	Ni-61 Weld	Silver Solder ^b
36	F ₂	6.3	—	0.002(0.001)	—	—	—	—	—	0.003(0.002)	nil(nil)	—
41	F ₂	26.6	—	—	—	—	—	—	—	0.001(nil)	0.001(0.001)	—
37	F ₂	7.4	—	—	—	—	—	—	—	—	—	0.153(0.064)
39	F ₂	7.0	—	—	—	—	0.006(0.008)	* (0.034)	0.044(0.067)	—	—	—
33	GeF ₄	28.0	—	0.002(0.001)	—	—	—	—	—	0.001(0.002)	0.002(0.001)	0.011(0.010)
35	GeF ₄ + F ₂	30.0	—	0.001(nil)	—	—	—	—	—	0.001(nil)	0.001(0.001)	0.052(0.017)
38	GeF ₄	28.2	—	—	—	—	0.001(nil)	0.001(0.001)	nil(nil)	—	—	—
42	GeF ₄ + F ₂	7.0	—	—	—	—	0.004(0.007)	* (0.031)	0.045(0.073)	—	—	—
43	AsF ₅	7.3	—	—	—	—	0.002 ^(d)	0.005(0.004)	0.002(0.001)	—	—	—
44	AsF ₅ + F ₂	7.4	—	—	—	—	0.006(0.010)	* (0.027)	0.031(0.050)	—	—	—
54	AsF ₅	7.2	—	nil ^(d)	—	—	—	—	—	nil(0.001)	0.001(0.001)	* (0.212)
55	AsF ₅ + F ₂	6.9	—	0.002(0.002)	—	—	—	—	—	0.002(0.003)	0.009(0.014)	0.265(0.104)
31	TeF ₆	6.9	* (0.283)	—	* (0.175)	* (0.033)	—	—	—	—	—	—
32	TeF ₆ + F ₂	5.3	0.002 (nil)	—	0.001(nil)	* (0.058)	—	—	—	—	—	—
52	TeF ₆	5.5	—	—	—	—	* (0.269)	* (0.542)	* (0.201)	—	—	—
56	TeF ₆ + F ₂	2.9	—	—	—	—	* (0.207)	* (0.942)	* (0.155)	—	—	—
45	SeF ₆	7.2	—	—	—	—	0.007(0.007)	0.016(0.014)	0.009(0.012)	—	—	—
46	SeF ₆ + F ₂	7.6	—	—	—	—	0.004(0.006)	* (0.036)	0.028(0.047)	—	—	—
48	MoF ₆	7.0	—	—	—	—	0.010(0.008)	0.030(0.014)	0.032(0.009)	—	—	—
49	MoF ₆ + F ₂	7.8	—	—	—	—	0.004(0.006)	* (0.022)	0.021(0.033)	—	—	—
60	BrF ₅	27.8	0.001(0.001)	—	0.002(0.001)	—	0.003(0.003)	—	—	—	0.001(0.002)	—
61	BrF ₅ + F ₂	7.8	0.005(0.012)	—	0.003(0.001)	—	0.011(0.007)	—	—	—	0.015(0.024)	—
62	NbF ₅	21.8	* (0.006)	—	* (0.002)	—	* (0.001)	—	—	—	* (0.007)	—
63	NbF ₅ + F ₂	5.1	0.003(0.004)	—	0.002 ^(d)	—	0.003(0.012)	—	—	—	0.003(0.006)	—
64	SbF ₅	7.2	* (0.064)	—	* (0.032)	—	0.006(0.007)	—	—	—	* (0.118)	—
65	SbF ₅ + F ₂	7.0	0.076(0.075)	—	* (0.021)	—	0.015(0.009)	—	—	—	0.531(0.356)	—
47	SF ₆	29.2	—	—	—	—	nil ^(d)	0.001(0.001)	nil(0.002)	—	—	—
50	UF ₆	7.6	—	—	—	—	0.007(0.008)	0.036(0.023)	0.017(0.021)	—	—	—
51	UF ₆ + F ₂	7.2	—	—	—	—	0.012(0.017)	* (0.046)	0.157(0.238)	—	—	—
57	UF ₆	7.2	—	* (0.010)	—	—	—	—	—	* (0.052)	* (0.067)	* (0.393)
58	UF ₆ + F ₂	7.0	—	0.004(0.004)	—	—	—	—	—	* (0.012)	* (0.071)	* (0.693)
66	UF ₆ + F ₂	7.0	0.006(0.010)	—	0.008(0.007)	* (0.196)	—	—	—	—	—	—

^a Corrosion rates calculated from the weight gain of the coupons, assuming that only NiF_2 formed on the surface of the entire coupon. Corrosion rates for the coupons containing areas of silver solder were calculated assuming that only AgF formed on the silver soldered surface, after the average corrosion rate of nickel-200 by the corrosive environment was deducted. The numbers in parentheses were calculated from weight loss data following immersion of the coupons in an equimolar KNO_3 - NaNO_3 salt bath at 500°C for $\frac{1}{2}$ hr, assuming complete removal of all scale. Corrosion rates are expressed in mil of metal reacted per hour of exposure. Rates reported as nil are less than 0.001 mil/hr.

^b American Platinum Works Division, Engelhard Industries, New Jersey Alloy No. 335. Composition: 56% Ag, 22% Cu, 17% Zn, 5% Sn, cadmium-free.

^c Excessive spalling of scale; weight gain data believed to be unreliable.

^d Corrosion scale not completely removed by KNO_3 - NaNO_3 bath at 500°C in $\frac{1}{2}$ hr.

^e No visible evidence of reaction was obtained although most of the coupons showed a slight weight loss after exposure.

TABLE II-20. RESULTS OF MICROSCOPIC EXAMINATION OF CORROSION SPECIMENS EXPOSED TO FISSION PRODUCT FLUORIDES AT 500°C.

Corrosive Environment	Reaction Time (hr)	Microscopic Examination						
		Nickel-200	Nickel-201	Monel	Inconel	Duranickel-301	HyMu-80	INOR-8
F ₂	6.3-7.4	—	No. I.G. ^a attack	—	—	No I.G. ^a attack	No I.G. ^a attack	No I.G. ^a attack
GeF ₄	28.0-28.2	—	About 25% of surface showed I.G. attack to 0.8 mil.	—	—	Isolated areas of I.G. attack to 0.4 mil.	Isolated areas of I.G. attack to 0.5 mil.	Isolated areas of I.G. attack to 0.4 mil.
GeF ₄ + F ₂	7.0-30.0	—	About 50% of surface showed I.G. attack to 0.8 mil. Isolated areas to 1.2 mils.	—	—	No I.G. attack	No I.G. attack	No I.G. attack
AsF ₅	7.2-7.3	—	Isolated areas of I.G. attack to 0.4 mil.	—	—	No I.G. attack	No I.G. attack	No I.G. attack
AsF ₅ + F ₂	6.9-7.4	—	No I.G. attack	—	—	No I.G. attack	No I.G. attack	No I.G. attack
TeF ₆	5.5-6.9	Uniform I.G. attack 0.4-1.2 mils. Isolated areas to 1.5 mils	—	No I.G. attack	No I.G. attack	No I.G. attack	No I.G. attack	No I.G. attack
TeF ₆ + F ₂	2.9-5.3	Uniform I.G. attack to 0.4 mil. Isolated areas to 1.2 mils.	—	Isolated areas of I.G. attack to 0.4 mil.	No I.G. attack	No I.G. attack	Surface very irregular. Uniform I.G. attack of 3 to 6 mils except at areas of high corrosion where I.G. attack was negligible.	No I.G. attack
SeF ₆	7.2	—	—	—	—	No I.G. attack	No I.G. attack	No I.G. attack
SeF ₆ + F ₂	7.6	—	—	—	—	<10% of surface has I.G. attack to 0.4 mil.	No I.G. attack	No U.G. attack
MoF ₆	7.0	—	—	—	—	Isolated areas of I.G. attack to 0.4 mil.	No I.G. attack	No I.G. attack
MoF ₆ + F ₂	7.8	—	—	—	—	No I.G. attack	No I.G. attack	No I.G. attack
BrF ₅	27.8	Uniform I.G. attack to 0.8 mil. Isolated areas to 1.0 mil.	—	About 50% of surface showed I.G. attack to 0.3 mil.	—	Isolated areas of I.G. attack to 0.4 mil.	—	—
BrF ₅ + F ₂	7.8	Uniform I.G. attack to 0.8 mil. Isolated areas to 1.6 mils.	—	About 10% of surface showed I.G. attack to 0.3 mil	—	Isolated areas of I.G. attack to 0.4 mil.	—	—

NbF ₅	21.8	About 50% of surface showed I.G. attack to 0.3 mil. Isolated areas to 1.0 mil.	—	Isolated areas of I.G. attack to 0.3 mil.	—	No I.G. attack	—	—
NbF ₅ + F ₂	5.1	Uniform I.G. attack to 0.6 mil. Isolated areas to 1.2 mils.	—	About 25% of surface showed very broad I.G. attack to 0.4 mil. Isolated areas to 0.8 mil.	—	About 25% of surface showed I.G. attack to 0.3 mil.	—	—
SbF ₅	7.2	Very irregular surface. About 50% of surface showed I.G. attack to 0.8 mil. Isolated areas to 1.2 mils	—	Very broad but fairly uniform I.G. attack to 0.6 mil. Isolated areas to 1.5 mils.	—	Isolated areas of I.G. attack to 0.3 mil.	—	—
SbF ₅ + F ₂	7.0	About 25% of surface showed I.G. attack to 0.5 mil. Isolated areas to 1.0 mil.	—	Very broad but fairly uniform I.G. attack to 0.6 mil. Isolated areas to 1.2 mils.	—	Isolated areas of I.G. attack to 0.4 mil.	—	—
SF ₆	29.2	—	—	—	—	Isolated areas of I.G. attack to 0.3 mil.	Uniform I.G. attack of 3-5 mils. Isolated areas to 7 mils.	No. I. G. attack
UF ₆	7.2-7.6	—	Isolated areas of I.G. attack to 0.4 mil.	—	—	No I.G. attack	About 50% of surface showed I.G. attack of 2-7 mils. The remaining 50% has no I.G. attack.	No I.G. attack
UF ₆ + F ₂	7.0-7.2	Uniform I.G. attack to 0.8 mil. Isolated areas to 1.5 mils	No I.G. attack	About 25% of surface showed I.G. attack to 0.4 mil. Isolated areas to 0.8 mil.	No. I.G. attack	No I.G. attack	About 50% of surface showed I.G. attack of 2-4 mils. The remaining 50% has no I.G. attack.	No I.G. attack

^a I.G. = intergranular.

corrosion is not well defined, the data appearing in Table II-20 may represent the maximum rates expected on long-term exposure.

Very little difference in corrosion rates was observed for nickel-200 and nickel-201. However, microscopic examination revealed that nickel-200 experienced much higher intergranular penetration than nickel-201 when exposed to identical environments.

Nickel and Monel exhibit the best overall resistance to corrosion by the volatile fission product fluorides individually and in the presence of fluorine at 500°C. Although the rates of corrosion of nickel-200 and Monel by TeF_6 alone at 500°C are relatively high, the presence of fluorine with TeF_6 significantly reduces these rates. It should be noted that the pressure of TeF_6 used in this study was about 100 mm, while the TeF_6 pressure expected in the fluid-bed reactor under process conditions is considerably less than 1 mm. The rates of corrosion of nickel and nickel alloys in anti-

mony pentafluoride alone and with fluorine at 500°C decrease in the order nickel-200, Monel, and Duranickel-301. The high rate of corrosion of Duranickel-301 in the presence of TeF_6 individually or with fluorine and the fact that the corrosion of Duranickel-301 by fluorine is at least a factor of two higher than the corrosion of nickel-200 or Monel limits the usefulness of Duranickel-301. Inconel, HyMu-80, and INOR-8 must be considered to be of questionable value for process considerations at this time because of their high rates of corrosion by TeF_6 and fluorine. The corrosion rates of the two types of nickel weld, namely, nickel-200 weld and nickel-61 weld, in the presence of fluorine at 500°C are both low. Nickel-200 weld appears to be superior to nickel-61 weld upon exposure to AsF_5 or UF_6 in the presence of fluorine. Nickel-61 weld is severely corroded by SbF_3 alone and in the presence of fluorine. A summary report on all phases of this work is being written.

B. ENGINEERING-SCALE INVESTIGATIONS OF FLUID-BED FLUORIDE VOLATILITY PROCESSES (A. A. JONKE)

1. Recovery of Uranium and Plutonium from Uranium Dioxide Fuels in the Engineering-scale Alpha Facility (N. LEVITZ, G. J. VOGEL, E. L. CARLS, I. KNUDSEN, J. V. NATALE, L. YOUNGBLOOD,⁵³ W. B. SEEFELDT, J. BISHOP, D. GROSVENOR, L. KOPPEL,⁵⁴ W. A. MURPHY, R. KINZLER, B. KULLEN, J. HEPPERLY, M. DEERWESTER, C. SCHOFFSTOLL, J. KINCINAS, W. KREMSNER, J. GERARD⁵⁵)

Process studies aimed at demonstrating the main steps of a fluid-bed fluoride volatility reprocessing scheme for $\text{UO}_2\text{-PuO}_2$ fuels were continued in the engineering-scale alpha facility. The primary objective of experiments performed in the facility is to investigate the possible difficulties in handling PuF_6 on an engineering scale. Further objectives are to determine the feasibility of fluoride volatility process flowsheets. Initial experiments involve the processing of $\text{UO}_2\text{-PuO}_2$ fuel containing synthetic fission products (F.P.); later experiments may be made with oxide fuel having low levels of fission product activity. The major processing steps of fluoride volatility processing are: decladding, fluorination of uranium and plutonium, distillation, purification of UF_6 , and thermal decomposition of PuF_6 to PuF_4 . The present alpha facility program is concerned with all steps except

decladding. Information on decladding has been reported in previous semiannual reports (ANL-7055, pp. 142-144; ANL-7125, pp. 91-93).

The engineering facility comprises two alpha boxes; the larger box contains the process equipment, while the smaller box contains off-gas scrubbers and other auxiliary equipment. Installed in the large box are two fluid-bed processing systems which have been operational with plutonium materials:

- The fluorinator for processing batches of oxide pellets to hexafluorides.

- The converter for (1) thermal decomposition⁵⁶ studies in separating plutonium as PuF_4 from $\text{UF}_6\text{-PuF}_6$ mixtures and (2) studies on the conversion of $\text{UF}_6\text{-PuF}_6$ mixtures to dense, homogeneous $\text{UO}_2\text{-PuO}_2$ particles.

⁵³ Temporary staff appointee from ORNL.

⁵⁴ Consultant from Purdue University.

⁵⁵ Co-op student from Purdue University.

⁵⁶ L. E. Treyvorrow, J. Fischer, and J. G. Riha, Laboratory Investigations in Support of Fluid-Bed Fluoride Volatility Processes. Part III. Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition, USAEC Report ANL-6762, August 1963.

The facility and these two processing systems have been described in a topical report.⁵⁷ A third processing system is a distillation unit (described in ANL-7055, pp. 138-141) for studies on UF_6 - PuF_6 mixtures; this unit has been erected in a mock-up area for testing (boil-up studies and calibrations). The unit will be installed in the alpha facility upon completion of these performance tests.

The initial program of studies in the facility with plutonium-bearing feed included three fluorination experiments (Pu-1, -2, and -3) and three thermal decomposition experiments (DUP-4, -5, and -6); the experiments in each group were made under similar conditions. These six experiments were followed by a clean-up fluorination (Pu-3a) designed to recover plutonium that had been deposited in equipment as a result of alpha decomposition and thermal decomposition. Information on plutonium behavior (extent of recovery, disposition, material balances) is being obtained to serve as a basis for evaluating fluoride volatility process flowsheets. As part of the program, efforts are continuing on the use of thermal conductivity cells for monitoring key components in the off-gas streams and as part of a process control scheme. Data reduction is being accomplished with the aid of computers.⁵⁸ Automatic data logging is undergoing preliminary testing.

In the fluorination step, batches of UO_2 - PuO_2 pellets containing inactive fission product oxides are processed by the two-zone oxidation-fluorination method to a mixed UF_6 - PuF_6 product. The reactions are conducted in an inert bed of sintered alumina which serves as a heat transfer medium. Oxygen (diluted with nitrogen) is fed at the bottom of the reactor and serves to convert the pellets to U_3O_8 - PuO_2 particulate fines. These fines are transported upward by the gas stream into the unhindered (pellet-free) alumina bed which extends about 2 ft above the pellet zone. Fluorine admitted in this upper zone converts these oxide fines to their corresponding hexafluorides. The hexafluoride product is collected in cold traps and then vapor-transferred to product receivers. The same alumina bed was reused for the entire series of fluorination experiments to achieve low waste volume-to-fuel ratios. For run evaluation, liquid and vapor samples of the hexafluoride product are obtained for

analysis, as well as samples of solids (alumina beds, NaF, activated alumina from traps).

The thermal decomposition experiments, performed in the converter, are exploratory in nature and are intended to show feasibility of a fluid-bed concept for this step. A relatively fine alumina bed has been used as a stand-in for the conceptual PuF_4 bed. With bed reuse, all the bed particles become coated with a uniform deposit of PuF_4 and therefore the bed material can be assumed to simulate a bed of PuF_4 . Mixed hexafluoride feed is metered as vapor and with added nitrogen serves as the fluidizing medium. The nondecomposed fraction (mainly UF_6) in the off-gas is collected continuously in the fluorinator cold traps and finally is transferred to product receivers. As in the case of the fluorination runs, run evaluation is based on analysis of alumina bed samples and feed and product hexafluoride liquid and vapor samples.

The first fluorination experiment and the first thermal decomposition experiment with plutonium materials were described in the preceding progress report (ANL-7125, pp. 86-91). The four remaining experiments in the current series have been completed, and the cleanup fluorination operations have started. Total plutonium material balance information is not yet available; however, experimental conditions and observations on the performance of the equipment are presented. Recent distillation column tests are also described.

a. FLUORINATION: OPERATING CONDITIONS, RESULTS, AND DISCUSSION

Experimental conditions and preliminary results are summarized in Table II-21. Data reported earlier on the first plutonium experiment are included to allow comparison of uranium and plutonium concentrations in the final alumina beds of the three runs. The fuel charge was nominally the same in each case, ~8.8 kg of 0.5 w/o PuO_2 - UO_2 pellets. The alumina charge was adjusted for successive experiments to provide for bed depletion due to sampling. Analysis of these bed samples establishes the extent of uranium and plutonium removal from the bed.

Run Duration. Each run comprises three fluorination periods: a two-zone oxidation-fluorination period during which the bulk (~80%) of the UF_6 is collected; a single-zone fluorination period, mainly for completing the uranium recovery; and, finally, a cleanup fluorination period, characterized by total fluorine recycle and gradually increasing bed temperatures to recover the plutonium values. As seen from Table II-21, duration of the separate fluorination periods varied from run to run. Run Pu-1 served as a base-line experiment. In run Pu-2 the two-zone fluorination period was

⁵⁷ G. J. Vogel, E. L. Carls, and W. J. Mecham, Engineering Development of Fluid-Bed Fluoride Volatility Processes, Part 5. Description of a Pilot-Scale Facility for Uranium Dioxide-Plutonium Dioxide Processing Studies, USAEC Report ANL-9001, December 1964.

⁵⁸ L. B. Koppel, P. G. Alfredson, L. J. Anastasia, I. E. Knudsen, and G. J. Vogel, A Generalized Computer Program for Flowsheet Calculation and Process Data Reduction, USAEC Report ANL-7197, April 1966.

TABLE II-21. OPERATING CONDITIONS AND RESULTS OF FLUORINATION RUNS.

Fuel Charge in each experiment: 8.8 kg of nominal 0.5 w/o $\text{PuO}_2\text{-UO}_2\text{-F.P.}$ pellets ($\frac{1}{2}$ -in. by $\frac{1}{2}$ -in. right cylinders, $\sim 90\%$ theoretical density), static height ~ 12 in.

Bed: 6.5–8.0 kg of nominal 48–100 mesh Alcoa T-61 alumina, static height about 2 ft above pellet bed. The same alumina bed was reused for each run.

Experiment	Duration (hr) of Given Period			Reactant Input during Two-Zone Reaction Period		Final Alumina Bed Analyses, (Grab Sample/Blend Sample ^b)	
	Two-zone oxidation-fluorination reaction	Single-zone fluorination	Cleanup fluorination ^a (total recycle)	O_2 (v/o)	F_2 (v/o)	Pu (w/o)	U (w/o)
Pu-1	8.0	4.2	8.3	~ 20		$\frac{0.02}{0.12}$	$\frac{0.02}{0.3}$
Pu-2	7.2	2.0	10.0	up to 25	9	$\frac{0.03}{0.03}$	$\frac{0.02}{0.024}$
Pu-3	15.5	2.0	13.5	10	10	$\frac{0.04}{0.22}$	$\frac{0.02}{3.2}$
Pu-3a ^c	—	—	6.0 (350 $\rightarrow$ 550°C)	—	—		
			15.0 (550°C)	—	—	$\frac{0.04}{0.06}$	$\frac{0.03}{0.03}$

^a See Figure II-18 for temperatures during cleanup-fluorination periods.

^b Blend sample taken from final bed after bed was withdrawn from reactor and blended.

^c Bed clean-up experiment; no fresh fuel added.

shortened to achieve increased hexafluoride production rates, while the two-zone period in run Pu-3 was intentionally extended and a higher oxygen concentration was used in the gas in an attempt to obtain more uniform hexafluoride production rates. In run Pu-3, no attempt was made to achieve high fluorine efficiencies and an excess of fluorine was maintained at all times to prevent reoccurrence of bed caking as observed in run Pu-2 (see following discussion).

Single-zone fluorination (fluorine admitted at the bottom of the reactor rather than at a side inlet) was started after about 80% of the hexafluoride had been collected in cold traps.

The cleanup fluorination period was sufficiently long to allow an adequate number of bed samples to be taken to provide accurate information on the rate of plutonium removal from the bed. Figure II-18 summarizes the results of these analyses and shows plutonium concentration in alumina as a function of time during the cleanup period. The curves for both runs Pu-1 and Pu-2 show the expected course of plutonium removal as the temperature was increased. The results from run Pu-3 show a low rate of plutonium removal from the bed during the 9-hr period in which the bed temperature was raised to 550°C. This was unexpected and may be related to the lower concentration of plutonium in the bed at the beginning of the cleanup

period, near 0.1 w/o for run Pu-3 as opposed to values of 0.2 w/o or greater for runs Pu-1 and -2. These data point out the need for developing an in-line detector for plutonium in the off-gas from the fluorinator so that process cycle time can be optimized.

Input Reactant Concentrations. The input oxygen concentration was increased to 25 v/o in the oxidation-fluorination step of run Pu-2 to achieve higher UF_6 production rates. However, soon after the start of the run, a large amount of U_3O_8 fines accumulated in the pellet bed, producing a high pressure differential across the bed. Apparently, the rate of oxidation during this period exceeded the rate of transport of the U_3O_8 fines from the pellet bed to the fluorination zone. Operations were continued, with only nitrogen supplied for fluidization, until pressures indicated that the U_3O_8 plug had been eliminated. Normal two-zone operations were then resumed, and high hexafluoride production rates of 5 to 6 lb/hr were sustained for periods of about one hour each; the average rate for the two-zone reaction period was about 2.6 lb/hr [equivalent to 51.2 lb/(hr) (sq ft)], about 20% higher than in run Pu-1. Fluorine efficiency during this period was about 66% as compared with about 50% for run Pu-1.

The lower oxygen input concentrations employed in run Pu-3 (~ 10 v/o as opposed to 25 v/o in run Pu-2) resulted in a somewhat more uniform hexafluoride

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FIG. II-18. Percent Plutonium in Alumina Grab Samples Removed from the Fluorinator during the Fluorination Cleanup Period.

(Runs Pu-1, Pu-2, and Pu-3)

production rate. No operating difficulties were observed in this run.

Average fluorine concentrations for the two-zone reaction periods in all three experiments were similar, approximately 10 v/o. Simple automatic control of fluorine input concentration is desired. A method based on the use of a signal from the off-gas fluorine analyzer (thermal conductivity cell) as the control element was evaluated during these runs and was partly successful. However, this technique is complicated by the long time constants of the system, and further development is required before the method can be perfected.

Elutriation of Fines. During each of the three fluorination experiments elutriation of plutonium-bearing fines (—200 mesh particles) to the upper portion of the fluid-bed reactor was observed. Indications of this situation were first observed when analyses of grab samples of the bed taken at the end of run Pu-1 while

the bed was fluidized showed significantly lower plutonium concentrations than analyses of samples taken from the final bed after the bed was withdrawn from the reactor and blended (see Table II-21). It appeared that plutonium-containing fines were retained on the sintered metal filters in the top of the reactor during fluidization. When fluidization was terminated as at the end of an experiment, these fines apparently returned (dropped) to the bed. The plutonium concentration in these fines (0.4 to 1.3 w/o, in run Pu-1) was significantly higher than in the bulk of the bed (0.06 w/o).

One mechanism which might lead to the production of plutonium fines would involve the reduction of PuF_6 by uranium oxide dust that has been elutriated from the bed. The plutonium would remain as a solid fluoride on the filters even in a high-fluorine-content stream because of the relatively low (<150°C) filter

temperatures. By increasing the temperature of the filters to 250°C to 275°C (as was done in run Pu-3a) it was possible to convert the PuF_4 fines to PuF_6 .

Filter blowback and rapping on the column would be expected to dislodge these fines. However, owing to the peculiar geometry of this reactor—each filter being housed in a separate 3½-in. dia. chamber—the fines dislodged from the filters may be quickly redeposited on the filters and not be returned to the bed and fluorinated to hexafluoride.

In order to provide more satisfactory operation of the filter blowback system, approximately 5 w/o alumina fines (<325 mesh) was added to the alumina bed in run Pu-2. It was expected that these fines would produce a filter cake on the sintered metal filters and that, upon blowback of the filters, the cake with accompanying plutonium fines would be returned in bulk to the bed. However, owing to (1) the high hexafluoride production rate in this run, with the concomitant absence of excess fluorine, and (2) temperatures of ~300°C in the disengaging zone, a small cake was produced at the bottom of the disengaging zone. The cake appeared to be primarily agglomerated fines, and was equivalent in weight to the quantity of alumina fines added to the bed. The agglomerated material was found to contain about 13% of the input plutonium. The concentrations of plutonium in the grab and blend samples for this run were similar, indicating that plutonium-containing fines were, in some way, being retained in the reactor above the bed.

Conditions were adjusted in run Pu-3 in an effort to eliminate some of these problems. The fluorine concentration in the gas stream above the bed was maintained at 7 v/o, and the disengaging zone temperature was raised to 450°C. On the basis of blowback tests performed in a Lucite column, the blowback frequency was reduced from once every minute to once every 8 min. This change was expected to allow the formation of a more substantial filter cake and more effective blowback action. Nevertheless, the final alumina bed from this run was contaminated with plutonium fines (0.22 w/o plutonium in the final bed, 0.04 w/o plutonium in a sample of the fluidized bed). The disengaging zone, though, was free of solids, indicating that the other changes in operating conditions (the use of excess fluorine and higher temperature) prevented agglomeration.

Further modifications in the operating procedure were incorporated during a subsequent cleanup fluorination of the bed (run Pu-3a). The fluidizing gas, nearly 100 v/o fluorine on total recycle, was interrupted at 30-min intervals throughout a major portion of the run; during these interruptions, the filters were blown back and the reactor walls were rapped in an

effort to return material from the upper sections of the reactor to the main reaction zone. Considerable plutonium was recovered, as is indicated by a final bed analysis of 0.06% plutonium (the starting bed for run Pu-3a contained 0.22 w/o plutonium). The grab samples showed a plutonium content of 0.04 w/o, which is lower than the final bed analysis and indicates that the intermittent gas stoppages were not frequent enough to allow complete cleanup of the fines. Results are nevertheless encouraging, and further operating modifications should eliminate the discrepancy in plutonium concentrations in the fluidized and final beds.

The final value of 0.03 w/o for uranium is equivalent to 99.9% recovery. The plutonium concentration in the final alumina bed (0.04 w/o) represented a 97% overall plutonium removal for the three uses of the bed material. Considering the fact that this was the first series of experiments, the results obtained are very encouraging.

Future Work. Recovery of residual plutonium from the entire system (reactors, pots, lines) by a recycle fluorination test at about 300°C is now in progress. For ease of operation NaF traps (rather than refrigerated condensers) have been installed to trap the PuF_6 by sorption from the separate sections of the equipment. Data on plutonium holdup as a function of equipment type (size, geometry) may be obtained. Material balances will be made upon completion of these tests. Further experimentation will probably employ the two-step scheme (ANL-7175, p. 52), oxidation followed by fluorination, rather than the two-zone reaction scheme used in the work reported here:

B. THERMAL DECOMPOSITION

Feasibility studies on the fluid-bed concept for separating plutonium from PuF_6 - UF_6 mixtures by thermal decomposition of PuF_6 to form solid PuF_4 were continued in the 2-in. dia. Inconel converter reactor (see system description in ANL-6925, pp. 136-139). The UF_6 passes through the system unreacted and is re-collected in cold traps. Ideally, the plutonium deposits on the surface of the bed particles as solid PuF_4 . In practice, PuF_4 would be used as the bed; for convenience in this work, a bed of alumina was used. Feed for these studies was provided by the fluorination experiments (see preceding section).

The initial thermal decomposition experiment (DUP-4) with a UF_6 - PuF_6 feed was reported in ANL-7125, pp. 90-91. Although the experiment was operationally successful, the input feed apparently contained little PuF_6 , and so the decomposition process itself could not be evaluated. The two recent experiments, runs DUP-5 and -6, complete the current exploratory program. These runs utilized the same

alumina starting bed, which was kept at 300°C during the runs. The final bed from run DUP-5 was used as the bed for run DUP-6. By accumulating PuF_4 in the bed, a closer simulation of a PuF_4 bed was achieved in run DUP-6.

The operating conditions for the three experiments are summarized along with the available results in Table II-22. The bed consisted of ~ 2.0 kg of -100 mesh Alcoa, Tabular T-61 alumina (static bed height about 16 in.). A material of relatively small particle size was chosen so that a low fluidizing gas velocity could be used, thus providing a high gas residence time in the bed. The superficial gas velocity was about 0.15 ft/sec which gave a calculated average residence time of ~ 12 sec. Approximately 9.7 kg of a UF_6 - PuF_6 mixture was fed from the 4-in. dia. feed pots in each case in about 8 hr; hexafluoride feed rates were about 20 g/min. The hexafluoride concentration in the feed stream was about 40 v/o. Sufficient nitrogen was added to the input stream to provide the proper fluidizing gas rate. The feed pot and lines were maintained at relatively low temperatures, $\sim 100^\circ\text{C}$ or below, in an effort to minimize thermal decomposition in these areas, yet to avoid condensation of the hexafluoride.

The exit gas, mainly UF_6 and nitrogen but also containing small quantities of PuF_6 and fluorine, was fed to the primary cold traps (those used with the fluorinator) for recovery of the hexafluorides. Vapor samples of the flowing gas stream, and liquid and vapor samples from the feed pot at the start and finish of the experiment and of the final UF_6 product

TABLE II-23. OFF-GAS AND UF_6 PRODUCT ANALYSES

Elapsed Sample Time (hr:min)	U/Pu in Off Gas ($\times 10^{-5}$)	U/Pu in UF_6 Product ($\times 10^{-5}$)
Run DUP-5		
1:18	1.3	
2:02	1.5	
3:01	1.2	
4:01	2.9	
5:01	2.0	
7:00	0.9	
8:00	—	
Average	1.4	
End of Run DUP-5		0.31
Run DUP-6		
1:05	0.96	
2:00	9.5	
3:02	4.6	
4:03	6.4	
5:00	18.0	
7:00	1.4	
7:34	6.6	
Average	6.8	
End of Run DUP-6		{ 7.6 (Liquid hexafluoride sample) 1.9 (Vapor hexafluoride sample)

TABLE II-22. OPERATING CONDITIONS AND RESULTS OF THERMAL DECOMPOSITION RUNS DUP-4, -5, -6

Bed Material: ~ 2.0 kg of -100 mesh Alcoa, T-61 alumina (~ 16 in. static height)

Superficial Fluidizing Gas Velocity: ~ 0.15 ft/sec

Total Hexafluoride Concentration in the Feed: ~ 40 v/o in nitrogen

Experiment	Run Duration (hr)	Average Hexafluoride Feed Rate (g/min)	Average Bed Temp. ($^\circ\text{C}$)	Final Bed Analysis ^a (w/o)			Off-Gas Analysis, Pu as w/o of UF_6	Pu Content of UF_6 Product (w/o)
				Pu	U	F		
DUP-4 ^b	9.6	17.9	350	~ 0.001	1.5	0.57	0.0003 ^c	0.0005
DUP-5	8.2	19.6	293	0.46	0.24	0.19	0.0007 ^c	0.0032
DUP-6	7.6	21.3	301	1.46	0.19	0.70	0.0004 ^c	0.0001

^a Fresh starting beds used in runs DUP-4 and DUP-5; final bed of DUP-5 used as starting bed of DUP-6.

^b This run was also described in ANL-7125, pp. 90-91.

^c Average value for six consecutive vapor samples (for run DUP-5) or seven samples (for runs DUP-4 and -6).

were taken, as well as bed samples. The presently available results are discussed below.

Results and Discussion. The degree of success in the decomposition step is reflected in the quantity of plutonium collected in the bed and in the absence of plutonium in the off-gas stream and the final UF_6 product. Material balances await results of accurate feed pot analyses, which will become available upon completion of current plutonium cleanup (fluorination) operations.

Off-gas samples from both runs DUP-5 and DUP-6 were found to contain low levels of plutonium; analysis of a sequence of samples for each run (see Table II-23), reported as uranium-to-plutonium ratio showed no trend of increasing or decreasing plutonium values; the results for liquid samples from the condensed UF_6 product provide confirmation of the low plutonium content. The spread in the values for the U/Pu ratios is considered to be acceptable at these low plutonium levels, <0.001 w/o plutonium in UF_6 .

Analysis of the bed showed a plutonium content of 0.46 w/o for run DUP-5; with further plutonium collection in run DUP-6, the level rose to 1.46 w/o. The uranium concentrations in the bed were 0.24 and 0.19

w/o, respectively, at the end of runs DUP-5 and DUP-6, as compared with 1.5 w/o at the end of the earlier experiment (DUP-4), which was performed at 350°C. The higher uranium content is, in part, attributed to the higher temperature and the associated higher rate of fluorination of the alumina by the UF_6 .

Based on an input feed composition calculated from the indicated plutonium accumulation in the bed and using the average off-gas U/Pu values, a separation efficiency for the decomposition process of ~99.9% was obtained for the final experiment. The bulk of the PuF_4 product formed in the converter appears to be deposited on the bed particles, since only a very small amount of PuF_4 was collected in a separate fines fraction. On the basis of these results it appears that the use of a fluid bed is a suitable technique for separating plutonium from UF_6 - PuF_6 mixtures by thermal decomposition.

c. DISTILLATION

Separation studies on uranium and plutonium hexafluoride systems are to be performed in the alpha facility. A distillation pilot plant (consisting basically of a still pot, a packed tower, and a condenser, and capable of batch or continuous operation) for this work is now

undergoing shakedown tests in a mock-up area. A description of the column and its main auxiliaries was presented earlier in ANL-7055, pp. 138-142. The objectives of these tests are to provide operational experience on the equipment, to verify that the various mechanical operations can be accomplished under simulated glovebox conditions, and to verify design calculations with a material that has a vapor pressure-temperature relationship close to that of UF_6 . Freon-113 (trichlorotrifluoroethane) has been found suitable for these tests.

Boilup Tests at Total Reflux. Tests were performed which involved the boilup of Freon-113 at various rates under total reflux to obtain information on column pressure drop, column flooding, adiabatic operation of the unit, and column holdup, and also to evaluate the operation of the condenser cooling system and column instrumentation.

Much of the data were obtained through the use of double-block thermal flowmeters (see Figure II-19) similar to those designed by Kessie.⁵⁹ The current design extends the range of this type of meter by the use of a larger tube size ($\frac{3}{8}$ -in. dia. rather than $\frac{1}{4}$ -in.) and the use of thermistors rather than thermocouples for greater sensitivity. In the design of the modified flowmeter, it was necessary to consider the problem of thermal decomposition of PuF_6 , and therefore the unit had to operate at relatively low temperatures (below 80°C), yet with a reasonably large temperature differential across the blocks. Calibrations of these units with nitrogen and Freon gave a nominal 10-15 mv output for flow rates of approximately 0.75 scfm with a 20°C differential imposed across the blocks. Calibrations with UF_6 , which are now in progress, will complete the current test program.

Column Pressure Drop and Flooding Point. The column was operated with Freon-113 to determine the effect of column pressure drop on Freon boilup rate and to estimate the flooding point. Figure II-20 shows the pressure drop across the packed column as a function of Freon boilup rate. The flooding point for Freon was determined to be 2450 lb/(hr) (sq ft). Since UF_6 has a liquid density higher than Freon-113, the flooding point for UF_6 is expected to be higher than the 2680 lb/(hr) (sq ft) reported by Ivins⁶⁰ for UF_6 distillations in similar, though smaller, equipment.

Column Holdup. The column (an 8-ft section of $\frac{1}{4}$ -in. schedule 80 pipe) is packed with single-turn nickel helices ($\frac{1}{8}$ -in. OD by 24 gauge), and the calculated void volume is 75%. The quantity of liquid held

⁵⁹ R. W. Kessie, Design and Construction of Thermal Flow Meters, ANL-6531, March 1962.

⁶⁰ R. Ivins, The Distillation of UF_6 and BrF_5 in a 0.5-inch Diameter Packed Column, ANL-6362.

p on the column packing at a boilup rate of 1880 lb/(hr) (sq ft) (75% of flooding) was determined by isolating the packed section of the column from the stillpot, vaporizing the liquid from the packing, and condensing the vapor. Approximately 390 cc of condensate was collected which corresponded to ~30% of the void volume of the column.

A separate test was made to determine the minimum volume of material in the still pot under which normal boilup could be maintained. The procedure involved boiling Freon from the column until a change in the heating characteristics of the column was observed. No change was noticed in flow rates or in temperatures until the volume of the material in the still pot dropped below ~300 cc. Adding this volume to the column holdup indicates that ~700 cc of material would be necessary in the equipment to provide wetting of the packing and heat transfer in the still pot. Assuming that in a batch distillation the still pot could be charged two-thirds full, it would therefore be possible to distill approximately 90% of the material from the column before performance of the column would be affected.

Adiabatic Operation of Equipment. The distillation column is covered with a 1½-in. layer of insulation, over which are mounted mantle-type heaters. Differential thermocouples are used to detect temperature differences across this layer of insulation during operation. The mantle heaters may be adjusted manually to minimize heat flow to or from the column and therefore an approach to adiabatic operation can be achieved. During the boilup tests, the average differential temperature between the column wall and the outer layer of insulation was held to less than 0.5°C.

Heat Losses, Wattmeter Calibration, and Condenser Coolant System Operation. Estimation of the heat balance on the column was made by comparing wattmeter readings with vapor boilup rates. A wattmeter is used to measure the input power to the still pot heaters. The correction for the heat loss from the still pot was determined so that the wattmeter readings could be used as a verification of the vapor boilup rate. This heat loss was approximately 30 watts. The vapor boilup rates indicated by thermal flowmeter measurements and those indicated by corrected wattmeter readings agreed within 10%. The quantity of heat transferred from the condensing vapor to the condenser cooling system (corrected for heat transfer from the enclosure) agreed well with the boilup rate measured by the thermal flowmeter. This agreement confirms that all of the vapor being boiled out of the still pot is passing through the vapor line to the column and not bypassing the thermal flowmeter through the liquid return line. It also indicates that little if any

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FIG. II-20. Freon Vapor Boilup Rate for Packed Column.

liquid is being entrained in the vapor stream and substantates that adiabatic operation of the column was achieved.

Recycle Operation. The distillation unit has the capability of recirculating a portion of the vapor from the condenser back to the still pot or from the still pot to the condenser region to simulate the operation of a continuous distillation unit at finite reflux ratios. Tests were performed to check the operation of the diaphragm pump under these recirculating conditions. Recycle of Freon condensate to two feed inlet points was also demonstrated. Results of these tests disclosed no operational problems with the exception of a need for rephasing the pump. This apparently is necessary because of the thermal expansion of the fluorolube oil between the diaphragms in the remote and pump heads.

Product Takeoff. A batch distillation with vapor product takeoff was simulated by drawing off a portion of the condenser vapor through the flow control valve located in the vapor takeoff line. No problems were encountered with this test, and the characteristics of the flow control valve were verified. The vapor takeoff line was also used successfully for intermittent purging of small amounts of noncondensables from the column.

Sampling. Provisions are made for sampling the va-

por from various locations in the distillation equipment. Samples are taken by trapping the material in an evacuated sphere between two valves and subsequently transferring the material by vacuum through a common manifold to removable sample tubes. To define the procedure and to confirm that no liquid was carried out with the vapor, samples were taken from all sampling points. In all cases the weight of the sample collected agreed with the calculated vapor weight.

Provisions are also made for obtaining a liquid sample from the still pot. This is accomplished by evacuating a section of line between two valves (one of which is connected to a down leg in the still pot) and then opening the valve to the still pot. Material trapped between the valves is allowed to drain into a removable sample tube. The down line is flushed be-

fore the next sample is taken, by pulling a "wash volume" through the line and subsequently back to the still pot.

Future Work. The distillation column is to be installed in the alpha facility upon completion of the current shakedown program. The unit was originally designed so that it could be taken apart in three sections and bagged-in vertically into the large alpha box. However, estimates show that considerable saving in time and manpower can be realized if the unit is transferred in one piece as assembled. On the basis of a mock-up test, this move appears mechanically feasible and details of this transfer are being evolved. Initial distillation work in the facility will be concerned with obtaining data for determining the height of packing equivalent to a theoretical plate.

2. Process Development Studies for Uranium Dioxide Fuels (D. RAMASWAMI, J. GABOR, D. RAUE, J. STRAND, W. KREMSNER)

The initial two steps in the fluid-bed fluoride volatility processes, currently under development, involve the separation of the cladding from the oxide fuels as the first step, and the conversion of the uranium and plutonium compounds to their volatile hexafluorides as the second step. Development studies on these two steps are being conducted with uranium-bearing fuels rather than with uranium-plutonium fuels because safety precautions required if plutonium were present would greatly complicate the operations.

a. PILOT PLANT STUDIES ON DECLADDING OF FUEL BUNDLES

The low-enriched uranium dioxide fuels are commonly clad with Zircaloy-2.⁶¹ Methods for chemically decladding Zircaloy-clad UO_2 fuel are being studied as part of the overall program on the development of fluoride volatility processes. The method currently under consideration involves the conversion of the cladding to volatile ZrCl_4 by reaction with HCl in a fluidized bed of alumina. The ZrCl_4 is then converted to solid oxide by reaction with steam in a separate fluid-bed reactor (see ANL-6900, p. 194). The oxide fuel is unaffected by the decladding reagent and remains in the halogenation reactor.

Previous demonstrations of this decladding technique were conducted in a pilot-scale facility which included a 6-in. dia. halogenation reactor, a 9-in. dia. packed-bed filter, and a 6-in. dia. pyrohydrolysis reactor (ANL-7125, pp. 91-93). It was observed in these

tests that the fuel bundle was gradually reacted from the bottom of the bundle to the top, and that the fuel bundle gradually settled into the bed as the lower portion was hydrochlorinated. The static bed of alumina in the 9-in. dia. filter was effective in retaining the uranium particulate generated during the decladding step.

The objectives of the current work were to determine (1) the effect of the presence of a fluidized bed of alumina on the hydrochlorination of Zircaloy-2 cladding, (2) the temperatures of fuel rods during the hydrochlorination step, and (3) the progress of decladding of a long fuel bundle in a shallow fluid bed.

(1) Decladding of Simulated Multi-Rod Fuel Bundles

A decladding run was conducted in the pilot-scale facility used in the previous studies (ANL-7125, pp. 91-93).

The fuel bundle comprised six rods, which were 70 in. long. In comparison, a "Type I" fuel bundle in the Dresden Reactor consists of 36 Zircaloy tubes (containing UO_2 pellets) 0.57 in. in diameter and 117 in. long, arranged in a square array.⁶²

Of the six rods used in the simulated bundle, two were solid Zircaloy-2 rods (0.5-in. dia.), and four were Zircaloy-2 tubes (0.53-in. ID, 0.59-in. OD) packed with UO_2 pellets. On one solid rod, 12 nickel-sheathed $\frac{1}{16}$ -in. dia. thermocouples were spot-welded 6 in. apart along the length, beginning at the bottom of the rod

⁶¹ Zircaloy-2 is a high-zirconium alloy that contains, in addition to zirconium, 1.5 w/o tin, 0.15 w/o iron, 0.10 w/o chromium, and 0.05 w/o nickel.

⁶² Directory of Nuclear Reactors, Vol. IV, Power Reactors. (Revised and Supplemented Edition of Vol. I), International Atomic Energy Agency, Vienna 1962, pp. 91-96.

The thermocouples were inserted in holes in the rod to a depth of $\frac{3}{16}$ in. All 12 thermocouples were brought out of the reactor through a single fitting, held together with Lava Sealant,⁶³ in the top flange of the disengaging chamber to minimize the temperature corrections usually needed for temperature measurements with thermocouples. The other solid rod was to be removed midway in the run to determine the extent of reaction along the rod length. The spacing between the fuel rods was similar to that (~ 0.14 in.) used for the Dresden fuel bundles.⁶² The total alloy charge was 3.4 kg, and the total UO_2 charge was 10.0 kg.

The alumina⁶⁴ charges were: 17.6 kg of $\frac{1}{2}$ - to $\frac{1}{4}$ -in. particles in the halogenation reactor as the support for the fuel bundle, 10.0 kg of 48–100 mesh particles as the fluid-bed material in the halogenation reactor, 15.0 kg of 14–48 mesh particles as the packed-bed filter material, and 10.0 kg of 48–100 mesh particles as the fluid-bed material for the pyrohydrolysis reactor. The respective static bed heights were 19 in. for the fuel-support bed, 12 in. for the fluid-bed material in the halogenation reactor, 11.5 in. for the packed-bed filter, and 12 in. for the fluid-bed material in the pyrohydrolysis reactor.

The temperatures of the fluid bed and the halogenation reactor wall (the entire height, including the disengaging zone) were maintained at $\sim 400^\circ\text{C}$. The operating conditions are summarized in Table II-24.

The concentration of HCl in the feed gas was controlled so that the temperatures of the Zircaloy rod would be less than 660°C . This temperature value was selected for reference since this same decladding technique may be used with fuel clad in aluminum which has a melting point of 660°C . At the start of the decladding step, the HCl concentration in the fluidizing gas was maintained at ~ 48 v/o HCl in nitrogen. The temperatures of the Zircaloy rod increased and then leveled off at a maximum value of about 520 to 540°C at which time the HCl concentration was increased to ~ 64 v/o. The maximum rod temperature then increased to approximately 640°C .

After two hours of hydrochlorination, the operation was interrupted while the Zircaloy rod with no thermocouples was taken out of the reactor; hydrochlorination was then resumed. The hydrochlorination was terminated after a total run time of 4.5 hr, when hydrogen concentration in the off-gas had decreased to a low equilibrium value, as indicated by the thermal conductivity cell apparatus, suggesting that hydrochlorination of the alloys was completed. The course

TABLE II-24. SUMMARY OF OPERATING CONDITIONS FOR DECLADDING A ZIRCALOY-2-CLAD URANIUM DIOXIDE FUEL BUNDLE

	Six-inch Diameter Halogenation Reactor	Nine-inch Diameter Packed-bed Filter	Six-inch Diameter Pyrohydrolysis Reactor
<i>Alumina Charges^a</i>			
Quantity (kg)	10.0 ^b	15.0	10.0
Mesh size	48 to 100	14 to 48	48 to 100
Static height in place (in.)	12.0	11.5	12.0
Temperature ($^\circ\text{C}$)	395	340	336
Gas velocity (ft/sec)	0.52	0.21	0.88

^a Sintered alumina manufactured by Aluminum Company of America.

^b In addition to this alumina, 17.6 kg of $\frac{1}{2}$ - to $\frac{1}{4}$ -in. alumina was charged to the halogenation reactor as a static-bed support (19 in.) for the fuel bundles.

of the reaction was also closely followed by comparing gamma-ray photographs of the contents of the reactor taken at regular intervals throughout the run. These film records indicated that during the run the tube bundle became shorter as the tube reacted with hydrogen chloride and disintegrated, and that finally the UO_2 pellets, which are unaffected by hydrogen chloride, accumulated in the bottom of the reactor. The time at which the gamma-ray photographs indicated complete reaction of the cladding was essentially the same as that indicated by thermal conductivity measurements.

Results and Discussion. The halogenation reactor, the packed-bed filter, and the pyrohydrolysis reactor operated smoothly during the entire period of hydrochlorination. The concentration of hydrogen chloride in the off-gas ranged from 32 to 64 v/o, whereas that in the feed gas ranged from 48 to 64 v/o indicating that, as expected, the entire length of the fuel bundle was exposed to gas with essentially the same composition.

Inspection of the Zircaloy rod removed from the reactor during the run indicated that the penetration rates varied along the length; the portion of the rod above the fluid bed was coated with a gray friable layer (2 to 10 mils thick). The penetration rates, measured after removing the gray layer, are plotted in Figure II-21. The penetration rates, calculated from dimensional changes, averaged 16 mils/hr for the portion of the Zircaloy rod immersed in the fluid bed and 34 mils/hr at the interface between the fluid bed and the gas phase 15 in. from the bottom of the rod. The highest rate of reaction occurred at the portion of the rod which was located above the fluid bed in the

⁶³ Natural magnesium silicate manufactured by Conax Corporation.

⁶⁴ Sintered alumina manufactured by Aluminum Company of America.

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FIG. II-21. Penetration Rate of a 0.5-Inch Diameter Zircaloy Rod Partially Immersed in a Fluidized Bed of Alumina. (Composition of the feed gas: 48 to 64 v/o HCl in nitrogen; Temperature of the fluid bed: $\sim 400^{\circ}\text{C}$; Temperature of the reactor wall: $\sim 400^{\circ}\text{C}$.)

zone where the diameter of the reactor increases from 6 in. to 12.5 in. (50 in. from the bottom of the rod). The penetration rates at remaining elevations in the gas phase ranged from 6 to 9 mils/hr.

Assuming that the reaction behavior of the Zircaloy tubes was similar to that observed on the solid Zircaloy rod, it would be expected that portions of the tubes exposed to the high reaction rates in the gas phase would disintegrate, thereby reducing the length of the fuel bundle. This was actually observed in the gamma-ray photographs taken during the run. It was shown in the film record that the fuel rods were broken at an elevation of ~ 50 in., and some fuel rod segments were held up in the disengaging zone of the reactor.

The high penetration at the interface of the fluid bed and gas phase may be attributed to the scrubbing of the metal by alumina particles owing to the breakup of gas bubbles. The high penetration rates at the expansion section between the 6-in. section and 12.5-in. section may be due to (a) the turbulence caused by the expansion, (b) the changes in flow patterns due to the internal fins in the disengaging chamber, and (c) the disengaging of fines. If this behavior is considered unacceptable, it may be necessary to incorporate certain changes in equipment design and operation in order to modify the heat-transfer and flow characteristics in the disengaging section of the reactor.

The temperature measurements of the Zircaloy rod,

the first of its kind in the development studies on the decladding step of the fluid-bed fluoride volatility process, showed that (a) in the fluid-bed zone, the temperatures were similar to those ($\sim 400^{\circ}\text{C}$) of the fluid bed, indicating that the heat transfer from the surface of the rod to the fluidized bed was good, and (b) in the gas phase above the bed, the temperature of the rod was much higher, up to 640°C , although the temperatures of the surrounding gas and reactor wall were 400°C , indicating that heat transfer from the rod to the surroundings was poor.

Conclusions. On the basis of these data on the penetration rates and temperature measurements, it is concluded that it is probably possible to declad long fuel bundles in shallow fluid beds. Experiments with larger tube bundles in larger reactors are needed to establish this point firmly.

No further experimental work is planned with the pilot-scale facility in view of the successful demonstration of decladding Zircaloy-clad low-enriched uranium dioxide bundles. The results obtained in this program to date are being summarized in the form of a topical report.

b. PROCESSING OF DECLAD URANIUM DIOXIDE

The fluid-bed fluoride volatility process is based on the ability to convert uranium and plutonium oxides to their hexafluorides. One method under investigation involves the oxidation of the fuel to a powdered mixture of U_3O_8 and PuO_2 followed by fluorination with either fluorine or bromine pentafluoride. Fluorination with BrF_5 results in the conversion of uranium to volatile UF_6 while plutonium is converted to non-volatile PuF_4 ; conversion of plutonium to PuF_6 is next accomplished in a separate step by reaction with fluorine. Other fluorination agents that might be used are bromine trifluoride or various mixtures of the fluorides. Exploratory tests are being conducted in a bench-scale fluid-bed facility to investigate the use of these fluorinating agents in the processing of UO_2 fuel. On the basis of the results of these tests, further evaluation of several of these agents will be made in an engineering-scale fluid-bed facility with specific emphasis on obtaining the engineering information needed for the design of the various equipment components of the fluorination system.

(1) Exploratory Tests on Fluorination with BrF_5 in a Bench-scale Fluid-bed Reactor System

Exploratory tests, conducted in a reactor having $1\frac{1}{2}$ -in. dia. fluid-bed section, involved the fluorination of U_3O_8 with BrF_5 in fluidized beds of alumina. The objectives of the tests were to determine (1) the effect

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FIG. II-22. Schematic Diagram of Reactor System for Exploratory Studies of BrF_5 Fluorination.

of temperature on the rate of fluorination of U_3O_8 , (2) the effect of BrF_5 concentration on the rate of fluorination of U_3O_8 , and (3) the feasibility of fluorination of UO_2 pellets.

Equipment and Procedures. The equipment used in these tests was that previously used for studies on the fluid-bed fluoride volatility process for the recovery of uranium from enriched uranium-zirconium alloy fuels.⁶⁵ Figure II-22 is a schematic diagram of the reactor system. The BrF_5 was supplied to the reactor from a cylindrical nickel still pot, 6-in. dia. by 8 in. high. The BrF_5 gas flow rate was measured by a thermal flowmeter, a Kel-F rotameter, and by still pot weight changes. The off-gas from the reactor was filtered by a packed bed of $-14 +28$ mesh alumina. The filter bed was maintained at the same temperature as the reactor bed. Four soda lime traps, each 4-in. OD by 24 in. high, with a total soda lime capacity of 12 kg were used for disposal of the off-gas.

For each run, 270 g of UO_2 pellets and 470 g of nominal 48 to 100 mesh alumina were charged to the reactor; 100 g of $-14 +28$ mesh alumina in the cone

section at the bottom of the reactor served as a support for the UO_2 pellets and as a fluidizing gas distributor. Periodically, fluid-bed samples were taken through a $1/4$ -in. sample line located $1\frac{1}{2}$ in. from the bottom of the fluid bed and were analyzed to determine the progress of the reaction.

Results and Discussion. Four tests (BrR-1 through BrR-4) were made at fluorination temperatures of 385, 290, 200, and 110°C to determine the minimum temperature for practical operation. Before fluorination, the UO_2 pellets were oxidized to form U_3O_8 fines at approximately 400°C with 30 v/o oxygen in nitrogen. (Run conditions are given on Table II-25.) The BrF_5 concentration for the four runs varied from 7.5 to 13.8 v/o in nitrogen.

The uranium concentrations in the fluidized alumina during the course of the fluorination are plotted in Figure II-23. Each point is based on analyses of samples withdrawn from the bed except for the final point which represents analysis of the bed after it was drained from the reactor. The data indicate that the lowest temperature at which practical fluorination rates are achieved is about 200°C ; the final bed at 200°C contained 0.17 w/o U.

Three tests (runs BrR-5, -6, and -7) were made to determine the effect of BrF_5 concentration on the rate

⁶⁵ D. Ramaswami, N. M. Levitz, J. T. Holmes, and A. A. Jonke, Engineering Development of Fluid-Bed Fluoride Volatility Processes. Part 1. Bench-Scale Investigation of a Process for Zirconium-Uranium Alloy Fuel, ANL-6829 (1964).

TABLE II-25. RUN CONDITIONS FOR DETERMINATION OF THE EFFECT OF TEMPERATURE ON FLUORINATION WITH BrF_5

Column Diameter: $1\frac{1}{2}$ in.
 Bed Charge: 270 g of UO_2 pellets (0.5-in. dia. by 0.5 in. long)
 470 g of nominal 48 to 100 mesh alumina^a
 Pellet-bed Depth: 1 in.
 Fluidized-bed Depth: 7 in. (static height)
 Diluent Gas: Nitrogen

	BrR-1	BrR-2	BrF-3	BrR-4
Oxidation				
Time, hr	3	3	3	3
Superficial gas velocity, ^b ft/sec	0.64	0.46	0.5	0.5
Oxygen concentration, v/o	28.2	33.4	30	30
Temperature, °C	440	415	400	385
Fluorination				
Time, hr	2.17	2.5	2.5	2.5
Superficial gas velocity, ^b ft/sec	0.70	0.55	0.5	0.5
BrF_5 concentration, v/o	7.5	9.2	13.8	11.9
Temperature, °C	385	290	200	110
Total BrF_5 feed, g	430	610	1135	1405

^a Type T-61, Tabular alumina, manufactured by Aluminum Company of America.

^b At operating temperature and 1-atm pressure.

of fluorination of U_3O_8 . These tests were conducted in two steps: oxidation of UO_2 pellets to U_3O_8 fines with 30 v/o oxygen in nitrogen at 400°C, followed by fluorination of the U_3O_8 to UF_6 with BrF_5 . The fluorination steps were conducted at different temperatures and BrF_5 concentrations: at 205°C with 29.4 v/o BrF_5 , at 230°C with 40.5 v/o BrF_5 , and at 175°C with 49.0 v/o BrF_5 (see Table II-26).

Interpretation of the results of these tests was complicated by the presence of significant amounts of uranium fines (from 7 to 35 g) in the packed-bed filters at the end of the runs; nevertheless, the results indicate, on the basis of the uranium concentration remaining in the bed, that the reaction rate is approximately proportional to the concentration of BrF_5 in the gas stream.

Three runs (BrR-10, -11, and -12) were made to determine the feasibility of direct fluorination of UO_2 pellets with BrF_5 by contacting 270 g of sintered, high density pellets with mixtures of BrF_5 and oxygen (see Table II-27). In a fourth run (BrR-14), the processing sequence involved a 1-hr oxidation period at 400°C with 30 v/o oxygen in nitrogen, followed by a fluorination period for 2 hr with a gas mixture consisting of 15.1 v/o BrF_5 and 31.2 v/o oxygen in nitrogen.

In BrR-10 (fluorinated at 300°C), only 5 g of UO_2 reacted in a 2-hr period. By increasing the fluorination temperature to 400°C, the quantity of UO_2 which

reacted in 2 hr increased to 49 g (~18% of the uranium charged). It was anticipated that in BrR-10, BrR-11, and BrR-12 the addition of oxygen to the BrF_5 gas stream would improve the fluorination rate by oxidizing the UO_2 to form U_3O_8 fines which would then be more readily converted to UF_6 . However, the pellets remained intact and exhibited only a small weight loss. The surfaces of the pellets were scraped off to determine if a protective layer of fluoride formed which prevented oxidation of the pellets. An X-ray diffraction analysis of the scrapings indicated no uranium compounds other than UO_2 . Apparently, the BrF_5 tends to inhibit oxidation of UO_2 . It appears that direct fluorination of UO_2 pellets with either BrF_5 or mixtures of BrF_5 and oxygen is not suitable as a process step.

Oxidation of the UO_2 pellets to U_3O_8 fines as in run BrR-14, was highly effective in producing a material reactive toward fluorination by BrF_5 . The 43 g of UO_2 pellet fragments recovered at the end of this run represented incomplete oxidation of the pellets of U_3O_8 .

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FIG. II-23. Uranium Concentration in Fluid-Bed Alumina during Fluorination with Bromine Pentafluoride. ($1\frac{1}{2}$ -in. dia. reactor; nominal 48 to 100 mesh alumina (470 g); 270 g UO_2 pellet charge.)

Comparing run BrR-14 with run BrR-1, it appears that the addition of oxygen to the BrF_5 does not markedly affect the rate of fluorination of U_3O_8 .

Future Work. The fluid-bed reactor will be modified by the installation of sintered metal filters in the disengaging section to prevent elutriation of uranium fines from the reactor.

Future tests will be concerned with determining the effect of the addition of fluorine to BrF_5 on the rate of fluorination of U_3O_8 . Also, additional tests will be made to obtain data at higher BrF_5 concentrations and to extend the range of previous data on the effect of temperature on the rate of fluorination of U_3O_8 .

(2) Development Studies with an Engineering-scale Fluid-bed Facility

Development studies are being made in an engineering-scale fluid-bed facility to obtain information needed for the design of various components of the fluorination system.

In the previous work (ANL-7125, pp. 93-95), the feasibility of sampling the beds for accountability purposes after oxidation of UO_2 pellets (some containing depleted uranium and the remainder normal uranium) was studied. Oxidation of batches of UO_2 pellets in fluidized beds of alumina at fluid-bed temperatures of $\sim 450^\circ\text{C}$ with feed gas compositions of ~ 20 v/o oxygen in nitrogen and at fluidizing-gas velocities of ~ 1.5 ft/sec proceeded smoothly and produced a mixture of U_3O_8 fines and alumina grain which was uniform with respect to the ratio of ^{235}U and ^{238}U in the uranium at the end of oxidation. The results of chemical analysis of samples of the fluid bed taken during the entire period (5.5 hr) of oxidation, suggested that fluid beds containing large quantities of oxide fines after oxidation can be sampled representatively for accountability purposes. Hydrofluorination of the U_3O_8 fines with HF to produce a mixture of UF_4 and UO_2F_2 was successfully carried out. High UF_6 production rates [65 to 80 lb UF_6 /(hr) (sq ft)] were achieved for 1- to 2-hr periods when large quantities of uranium fines were present in the beds by reaction of uranium oxides or fluorides with fluorine.

In the current work, four additional runs were made on oxidation-fluorination reactions to confirm previous data on the various aspects of these reactions. The objectives of the current work were to determine

- (1) The effect of the prefluorination temperature of the fluidized bed of alumina on fluoride uptake by the alumina bed,
- (2) The effect of the duration of oxidation (when UO_2 pellets with two different uranium isotope ratios are oxidized) on the ratio of ^{235}U to ^{238}U in the uranium of the fluid-bed samples,

TABLE II-26. RUN CONDITIONS FOR DETERMINATION OF THE EFFECT OF BrF_5 CONCENTRATION ON FLUORINATION OF U_3O_8

Column Diameter:	1½ in.		
Bed Charge:	270 g of UO_2 pellets (0.5-in. dia. by 0.5 in. long) 470 g of nominal 48 to 100 mesh alumina ^a		
Pellet-bed Depth:	1 in.		
Fluidized-bed Depth:	7 in. (static height)		
Diluent Gas:	Nitrogen		
	BrR-5	BrR-6	BrR-7
Oxidation			
Time, hr	3	3	3
Superficial gas velocity, ^b ft/sec	0.5	0.5	0.5
Oxygen concentration, v/o	30	30	30
Temperature, °C	410	400	400
Fluorination			
Time, hr	0.83	0.58	0.50
Superficial gas velocity, ^b ft/sec	0.5	0.5	0.5
BrF_5 concentration, v/o	29.4	40.5	49.0
Temperature, °C	205	230	175
Total BrF_5 feed, g	850	700	960

^a Type T-61, Tabular alumina, manufactured by Aluminum Company of America.

^b At operating temperature and 1 atm.

TABLE II-27. PROCESSING CONDITIONS FOR THE DIRECT FLUORINATION OF UO_2 PELLETS WITH BrF_5

Column Diameter:	1½ in.			
Bed Charge:	270 g of UO_2 pellets (0.5-in. dia. by 0.5 in. long) 470 g of nominal 48 to 100 mesh alumina ^a			
Pellet-bed Depth:	1 in.			
Fluidized-bed Depth:	7 in. (static height)			
Diluent Gas:	Nitrogen			
	BrR-10	BrR-11	BrR-12	BrR-14 ^b
Time, hr	2	2	2	2
Superficial gas velocity, ^c ft/sec	0.55	0.52	0.55	0.55
BrF_5 concentration, v/o	13.9	11.7	18.6	15.1
Oxygen concentration, v/o	30	30	27.2	31.2
Temperature, °C	300	410	410	400
Total BrF_5 feed, g	810	600	1010	810
UO_2 reacted, g	5	49	46	227

^a Type T-61, Tabular alumina, manufactured by Aluminum Company of America.

^b Before fluorination, the pellets were oxidized for 1 hr at 400°C with 30 v/o oxygen in nitrogen and a fluidizing gas velocity of 0.5 ft/sec.

^c At operating temperature and 1 atm pressure.

- (3) The effect of the use of fragmented UO_2 pellets (simulating irradiation damage of sintered oxide fuel) on the progress of oxidation, and
- (4) Satisfactory operating conditions for fluorinating large quantities of uranium oxide fines in a fluid bed.

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FIG. II-24. Effect of Oxidation Time on the Ratio of ^{235}U to ^{238}U in Uranium of the Fluid-Bed Samples. (Uranium dioxide charge: 2.2 kg of depleted pellets, 2.2 kg of normal pellets; alumina charge: 6.85 kg of -60 mesh sintered alumina; oxidation conditions: temperature = 440°C , feed gas composition = 21 v/o oxygen in nitrogen.)

Equipment. The equipment consisted of a 3-in. dia. nickel fluid-bed reactor and auxiliary equipment as described in ANL-7125, pp. 93-95. Additional thermocouples were installed in the fluid-bed reactor section to obtain an accurate temperature profile of the fluid bed, and additional pressure taps and pressure transmitters were installed to record differential pressures across segments of the fluid bed. The differential pressure measurements were employed to observe changes in the quality of fluidization as the UO_2 pellets were oxidized to U_3O_8 fines and as the U_3O_8 fines were converted to UF_6 during fluorination.

Exposure of Alumina Fluid Bed to Fluorine. A test was performed in the 3-in. dia. fluid-bed reactor to determine the effect of prefluorination temperature on the extent of conversion of alumina-bed material to fluoride. The alumina bed was exposed to 65 v/o fluorine at 20, 450, and 550°C for 4 hr at each temperature level. The gas velocity in the fluid bed was ~ 0.45 ft/sec for the room-temperature exposure and 0.9 ft/sec at the higher temperatures.

Results of chemical analyses of samples taken from the fluid bed during fluorination indicated that the concentration of fluoride in the bed increases with an increase in temperature and approaches an equilibrium value at a given temperature level after about 2 hr.

The concentrations in the alumina bed at the end of each interval were 0.09, 0.6, and 1.2 w/o, respectively. Prefluorination of the alumina bed at 550°C with high concentrations of fluorine would reduce the conversion of the alumina to fluoride during the fluorination of uranium fuel materials.

Oxidation of UO_2 to U_3O_8 Fines and Sampling of the Bed. One advantage of oxidizing UO_2 fuel to U_3O_8 fines prior to fluorination is that this process step may allow the taking of samples of the fluid-bed material which are representative of the fuel charge. If this should be the case, the problem of obtaining an accountability sample that would have a plutonium content representative of the PuO_2 content of the UO_2 fuel charge would be resolved. To obtain information on the possible distribution of plutonium in the fluid bed after oxidation, UO_2 pellets were used which contained ^{235}U in concentrations approximating the plutonium concentrations expected in UO_2 - PuO_2 fuels. The assumption was made in these experiments that the distribution behaviors of ^{235}U and plutonium are the same.

Uranium dioxide pellets of two enrichments were used. In two experiments, 6-in. deep beds of UO_2 pellets (4.4 kg total), consisting of equal quantities of depleted (0.2198% ^{235}U) and normal (0.7218% ^{235}U) UO_2 pellets, were charged to the reactor. The pellets were fragmented to $-0.5 + 0.132$ in. particles prior to charging to the reactor to simulate irradiation damage of sintered oxide fuel. Approximately 6.9 kg of sintered alumina,⁶⁶ equivalent to a static-bed height of 30 in., was used as the fluid-bed material. In one experiment (reported in ANL-7125, pp. 93-95), the alumina was -100 mesh size, in another, -60 mesh. The fluidizing gas, 13 to 19 v/o oxygen in nitrogen, was fed at a superficial velocity of 1.5 ft/sec. Oxidative pulverization of the pellets was carried out at 450°C and was completed in 5.5 hr in the first experiment and in 11 hr in the second. Two additional experiments involving the oxidation of different proportions of depleted and normal UO_2 pellets were performed. In one case, 0.22 kg of depleted UO_2 pellets and 1.98 kg of normal pellets was oxidized. The other experiment involved the oxidation of 0.02 kg of depleted pellets and 1.98 kg of normal pellets. In each experiment, 2.91 kg of -60 mesh alumina was used as the fluid-bed material. Oxidation conditions were the same as in the other experiments.

In the experiment in which the oxidation was carried out for 11 hr, analyses of bed samples taken periodically throughout the run (see Figure II-24) indicated that the uranium in the samples remains homogeneous with respect to ^{235}U content after 5 hr. The experiments involving the oxidation of unequal amounts of

⁶⁶ Sintered alumina, type T-61, manufactured by Alcoa.

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FIG. II-25. Uranium Hexafluoride Production Rates.

depleted and normal oxide pellets also showed homogeneous distribution of ^{235}U after 5.5 hr of oxidation.

Within the range of fluid-bed particle sizes used in these experiments, it appears that the homogeneity of the uranium isotopes in the U_3O_8 powder is unaffected by the bed-particle size. The distribution of U_3O_8 powder in the fluid bed also appeared to be unaffected by the size of the fluid-bed particles. These results indicate that it is reasonable to expect that plutonium, when present in low concentrations in uranium, will also be distributed homogeneously within the uranium fraction after oxidation in the fluid bed, and that it may be possible to employ sampling of the fluid bed for accountability purposes.

No difficulties were observed during oxidation of fragmented pellets; the processing step proceeded as smoothly as in the oxidation of cylindrical pellets.

Fluorination of U_3O_8 Fines. Four experiments were performed to determine satisfactory operating conditions for fluorinating large quantities of uranium oxide fines in a fluid bed. At the end of the first experiment, minor portion of the final bed was found to be caked. Analyses of the data from this experiment and previous experiments involving fluorination of uranium oxide fines suggest that the formation of a cake might result

from a combination of high temperature in the fluid bed, low gas velocity in the bed, and low concentrations of fluorine in the off-gas stream. An increase of the fluorine concentration in the off-gas stream could be achieved by reducing the fluorination temperature or an increase in gas velocity. These approaches were successfully applied in the other three experiments.

The operating procedure for a typical experiment in this group of three for the period when large quantities of fines were present was: 1 hr at 350°C with 6 to 10 v/o fluorine in nitrogen, 1.5 hr at 350 to 400°C with 15 v/o fluorine, 1.5 hr with 20 to 30 v/o fluorine at 400 to 475°C. The fluidizing gas velocity was maintained at 0.9 to 1.5 ft/sec. The fluorine concentration in the off-gas stream was between 3 and 5 v/o. After the bulk of uranium oxide fines had been fluorinated, the final oxide fines were contacted with 95 v/o fluorine for 1 hr at 475°C with a gas velocity of 0.25 ft/sec. Average uranium hexafluoride production rates of 50 lb/(hr) (sq ft) were achieved during the first 2½ hr of fluorination with maximum rates of 80 lb/(hr) (sq ft). No temperature excursions were observed. The results of a typical experiment are shown in Figure II-25. In

all cases, the alumina bed material was free-flowing at the end of the experiment.

Future Work. Modifications of equipment to handle

BrF_5 in the engineering-scale fluid-bed unit have been initiated to allow development studies on the use of BrF_5 .

3. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride

(R. KESSIE, D. RAMASWAMI, L. MAREK)

The high volatility of PuF_6 combined with the high toxicity of plutonium requires special techniques to assure its removal from ventilation air. At moisture concentrations normally present in the atmosphere, PuF_6 reacts with the moisture to produce an aerosol of solid particles of PuO_2F_2 by the reaction:

At low moisture concentrations, however, this reaction does not occur to a measurable extent in the gas phase but occurs on solid surfaces exposed to the reactant mixture.

In previous work, which has been reported in detail,⁶⁷ the surface reaction kinetics was measured in packed beds of glass spheres. Using the reaction rates measured in the packed bed experiments, it was estimated that AEC-type filters would be highly effective in promoting the surface reaction owing to the large internal surface of these filters. At very low moisture concentrations, the efficiency of the filters would be less; however, this situation could be avoided by humidifying the air.

In the case of aerosol formation, it was shown⁶⁷ that the diameters of more than 90% of all particles in the aerosol were less than 0.1 micron. When a gas stream containing an aerosol of PuO_2F_2 was passed through two high-efficiency AEC-type filters in series at 40% of rated flow, the plutonium concentration of the aerosol in the gas stream was reduced by 10^{-6} to 10^{-9} .

Experiments currently under way are designed to measure the penetration of high-efficiency filters resulting from both incomplete surface reaction and particulate penetration. In these experiments, gas containing plutonium aerosol is passed through several filters in series and the penetration of the filters is determined by analyses of the plutonium on the filters. Initial experiments have resulted in samples with very low levels of plutonium concentration; precise deter-

minations will require development of analytical techniques. As a result no data are available at this time.

In order to define and understand the mechanisms involved in the filtration of fine particulate solids such as plutonyl fluoride, numerical analyses of basic equations describing the flow and filtration behavior of aerosols are being performed. The theory on filtration of very small particles involves principally the mechanisms of diffusion (Brownian motion) and of interception. These theories are based on random walk distances to the fiber surface in a laminar-flow field.⁶⁸ In applying this theory to filtration by the high-efficiency filters, it is necessary to assume that a laminar-flow field exists around the filter fibers; this assumption results in error since it neglects the effect of slip velocity on the flow field around the fiber. Slip velocity is the velocity of the fluid in contact with the surface and is due to the molecular structure of the fluid. A first approximation of the slip velocity indicates that it will be at least one-half the velocity occurring one molecular mean free path away from the surface. The radius of over 40% of fibers in the high-efficiency filters (AEC type) is smaller than the molecular mean free path of air. This means that the assumption of a laminar-flow field around the fibers would be a poor approximation of the true situation. As a result of the slip velocity, inertial forces of the flowing fluid (air) will increase the slip velocity to a value such that it could approach or exceed the free stream velocity, as in potential flow (nonviscous approximation to turbulent flow), even though the Reynolds number is much less than unity, indicating laminar flow around the fibers. Since the slip velocity apparently is significant in this case, both the diffusion and interception mechanisms would be more effective in high-efficiency filters than is indicated by the current theory. An attempt at improving the theory by numerical methods is being made in the current work.

4. Bench-Scale Studies with Irradiated Fuels (A. CHILENSKAS, G. POTTS)

A program demonstrating the fluid-bed volatility process with irradiated fuel materials is in progress.

⁶⁷ R. Kessie and D. Ramaswami, Removal of Plutonium Hexafluoride from Cell Exhaust Air by Hydrolysis and Filtration, ANL-7066, December 1965.

Experiments are being conducted in a 1½-in. dia reactor installed in the senior cave facility of the

⁶⁸ "The Collected Works of Irving Langmuir," C. G. Suits (Ed.), Vol. 10, p. 394, Report on Smokes and Filters, Pergamon Press, N. Y., 1961.

Chemical Engineering Division. The aims of the program are to obtain information regarding (1) the distribution of fission products during the various process steps, (2) decontamination factors that may be realized, and (3) the effects, if any, of irradiation and the presence of fission products on uranium and plutonium recovery. The work with irradiated metal alloy fuels has been completed and a report⁶⁹ detailing the results is in preparation. Four experiments (SCAX-1, -2, and -3 and SCAV-1) with irradiated, low-enriched oxide fuel materials have been completed and preliminary results are presented herein.

The apparatus and procedures for these experiments were similar to those employed for processing irradiated uranium metal alloy fuels and have been previously described in ANL-7055, p. 156 and ANL-7125, pp. 98-99. It should be noted that these four oxide runs employed a packed-bed filter containing alumina particles downstream of the fluid-bed reactor. Modifications to the apparatus have been undertaken so that future runs will be made with a sintered metal filter located in a separate chamber above the bed.

a. PROCESSING IRRADIATED UO_2 PELLETS USING A HF/O_2 STEP FOLLOWED BY A FLUORINATION STEP—RUNS SCAX-1 AND -2

Duplicate runs (SCAX-1 and -2) were made using irradiated UO_2 pellets which had been mechanically dekad. The first process step involved pulverization of the UO_2 to UO_2F_2 and UF_4 fines using 48 v/o HF in oxygen at 400°C. The second step utilized 2 to 20 v/o fluorine in nitrogen to volatilize the uranium as UF_6 which was collected in a product trap containing NaF pellets. The results of these two runs are shown in Table II-28. The values are each expressed as percent of the charge and are averages for the two runs except where otherwise indicated. The principal volatile fission products during the HF/O_2 step which appeared in the condenser and scrubber were antimony, molybdenum, and technetium. Ruthenium showed only slight volatility. Examination of the activities found in the NaF and activated alumina traps showed the principal volatiles during fluorination were ruthenium, niobium, and antimony. Ruthenium was shown to be only partly removed from the off-gas stream by the series of NaF traps; 12.8 percent of the ruthenium charged was found on the activated alumina trap. About 45% of the ruthenium present in the UO_2 charge volatilized in the fluorination step, compared with less than 1% for the metal alloy fuels in which the fluorina-

tion conditions were more severe (ANL-7055, p. 159). This result suggests that the HF-oxygen pretreatment may produce a ruthenium species which upon fluorination with fluorine is readily converted to a volatile compound.

Material balances and decontamination factors are shown in Table II-29. The activity recoveries ranged from 46% for the gross gamma to 115% for strontium. The low values for gamma and cesium activities are primarily due to a loss of cesium during analysis of the reactor bed and filter bed. Sample dissolution procedures included a fusion of the alumina bed with 1:1 sodium carbonate-sodium borate flux at about 1000°C. Considerable loss of cesium (volatilization of up to 60% of the cesium in some samples) has been shown to occur. Analytical procedures to circumvent this situation are being developed. Since it is known that some fission products tend to deposit on the surfaces of process equipment, material balances of >70%, achieved in these runs for all activities except cesium and ruthenium, are considered to be satisfactory for this scale of operation. Some decontamination of equipment components is being undertaken to investigate the extent to which preferential deposition may occur.

Decontamination factors (DF) for uranium are also shown in Table II-29. These factors were calculated in two ways: in one method, the decontamination factor was calculated by assuming that all overheads from the reactor are condensed with the uranium with no traps present; in the second method, the decontamination factor included the effect of a 400°C NaF trap interposed between the reactor and the 100°C NaF trap. As is shown, without cleanup in a 400°C NaF cleanup trap, the decontamination from gross β and γ activities was about 20 while a DF of about 70 was achieved with cleanup in this NaF trap. Improvement factors⁷⁰ in the DF from gross β , γ , ruthenium, antimony, and zirconium ranged from 3.4 to 5 while an improvement factor of 940 was achieved for niobium. Little or no improvement was noted for molybdenum and technetium.

The gamma compositions of the various process streams are given in Table II-30. As is shown by this table, the preponderant gamma activity of the uranium product, obtained when the 400°C NaF trap was employed, is due to ^{106}Ru (82.5%) with ^{137}Cs (3.8%) the next largest contributor. Improvements in filtration, such as that obtainable by the use of sintered metal filters, and improved ruthenium trapping by the use of more efficient NaF traps would result in additional decontamination such that final purification steps (e.g., distillation) would be possible in lightly shielded equipment.

⁷⁰ The ratio of DF with 400°C NaF cleanup to DF without 400°C NaF cleanup.

⁶⁹ A. A. Chilenskas and K. S. Turner, Engineering Development of Fluid-Bed Fluoride Volatility Processes. Part 10. Bench-Scale Studies on Irradiated Highly Enriched Uranium Alloy Fuels, ANL-6994 (1966).

TABLE II-28. DISTRIBUTION OF URANIUM AND FISSION PRODUCTS FOLLOWING FLUID-BED VOLATILITY PROCESSING OF IRRADIATED UO_2 —RUNS SCAX-1 AND -2

Reactor Charge

50 g Irradiated UO_2 , 20,000 Mwd/t, cooled 22 months; γ 5.5×10^{12} c/m; β 5.5×10^{12} c/m; $\sim 5.5 \times 10^{13}$ d/m (at time of charging); 700 g granular alumina, 14-100 mesh

Process Conditions

HF/ O_2 Step: Reactor, 400°C; Filter, 350°C; 4 hr; 48 v/o HF in O_2 ; 5.5 liters/min NTP

F_2 Step: Reactor, 405-450°C; Filter, 350°C; 3 hr; 2-20 v/o F_2 in N_2 ; 5 liters/min NTP

Percent of Charge^a

^a Each value is the average for runs SCAX-1 and -2 except where stated otherwise.

^b Analyses known to be low. A new analytical technique is under development.

^c Analysis from one run only (SCAX-1).

^d As determined by gamma spectrometric analyses.

^e Analyzed after the two runs were completed. The values listed are each one-half of total found by analysis.

b. PROCESSING IRRADIATED ZIRCALOY-CLAD UO_2 USING A HCl STEP, AN OXIDATION STEP, AND A FLUORINATION STEP—RUN SCAX-3

Two runs were performed consecutively, the first (SCAX-3) with an irradiated charge and the second (SCIX-2) with a nonirradiated charge, and the gamma levels in each vessel at the end of the runs were compared to determine carryover of fission products in the apparatus between runs. Prior to run SCAX-3, the reactor and filter were cleaned by brushing the equipment and evacuating deposited fines; the scrubber and condenser were washed with acid solutions. The results for the run with an irradiated Zircaloy-clad UO_2 charge are shown in Table II-31. Between runs, alu-

mina and the contents of each trap were replaced with fresh material. Then, a run (SCIX-2) was made using a nonirradiated UO_2 charge, and the gamma contamination of the cold-trap product and other samples of interest was determined. Since the results for the inactive run showed a high level of contamination of the equipment, individual fission product analyses were not undertaken for the active run.

The gamma level of the cold trap after the inactive run was about 10% of that after the active run; hence the decontamination factors of 28 for beta and 26 for gamma activities in run SCAX-3 are representative for this processing scheme. The gross beta and gamma values in the condenser and scrubber are also representative since the residual values found after the in-

active run were about 5% of those found after the active run. The reactor, filter, activated alumina trap,

and nickel ball trap all had residual values after run SCIX-2 that were between 33 and 125% of those for the active run; these values are too uncertain to allow reliable interpretation.

TABLE II-29. MATERIAL BALANCES AND DECONTAMINATION FACTORS (AVERAGE VALUES) FOR RUNS SCAX-1 AND -2

Activity	Percent of Charge Recovered	Decontamination Factor ^a		DF Improvement Factor ^b
		Without NaF cleanup	With 400°C NaF cleanup	
U	86	—	—	—
β	70	24	81	3.4
γ	46 ^c	17	59	3.4
Cs	54 ^c	—	720	—
Sr	115	—	400	—
TRE	73	—	—	—
Sb	80	26	130	5
Ru	59	2	7	3.5
Zr	73	450	2.2×10^3	4.9
Nb	73	5	4.7×10^3	940
Mo	108	—	0.84	—
Tc	84	—	1.1	—

^a Decontamination Factor

$$= \frac{\text{activity per gram U in the charge}}{\text{activity per gram U in the product}}$$

^b DF Improvement Factor

$$= \frac{\text{DF with 400°C NaF Cleanup}}{\text{DF without 400°C NaF Cleanup}}$$

^c These values are known to be low owing to loss of cesium during reactor and filter bed analyses. New analysis for Cs is under development.

c. PROCESSING IRRADIATED AND NONIRRADIATED ZIRCALOY-CLAD $\text{UO}_2\text{-PuO}_2$, USING A HCl STEP, AN O_2/F_2 STEP, AND A FLUORINATION STEP

Two runs with mixed $\text{UO}_2\text{-PuO}_2$ feed were performed to determine the distribution of fission product residues in the apparatus and to establish the level of plutonium retention in the reactor and filter beds. The mixed oxide for the run (SCIV-2) with a nonirradiated charge was manufactured from the same batch as the irradiated fuel used in run SCAV-1 and was processed under the same conditions as were used in the run with irradiated fuel. Material in all process vessels and traps was replaced with fresh material between runs. The results for the two runs are presented in Table II-32. It can be seen in Table II-32 that the activity levels found in the condenser and scrubber for the inactive run were higher than in the subsequent run, with irradiated feed (SCAV-1), and therefore the values found for the activity movement to the condenser and scrubber for the hot run are apt to be high. The other residual values found for the inactive run are lower than the values for the active run and show that the residual activities in the apparatus for these samples are of minor importance.

TABLE II-30. GAMMA COMPOSITIONS OF THE PROCESS STREAMS FOR RUNS SCAX-1 AND -2 (AVERAGE VALUES)
For normalized time of analysis

Process Stream	Gross γ (c/m)	Percent of Gross Gamma Counts					
		Ru	Sb	Cs	Zr	Nb	Remainder
Charge	4.3×10^{12}	8.7	1.2	52	1.5	2.7	33.9 ^a
Reactor bed	1.0×10^{12}	1.8	1.1	75	3.0	3.8	15.3 ^a
Filter bed	7.5×10^{11}	4.5	1.8	59	2.7	4.0	28.0 ^a
400°C NaF	1.6×10^{11}	79	0.85	—	0.5	13	6.7 ^b
100°C NaF	5.8×10^8	9	57	76	0.9	0.9	>100% ^c
25°C NaF	2.3×10^9	1.1 ^d	9 ^d	116 ^d	1.5 ^d	0.8	>100% ^c
Condenser	1.1×10^{10}	35	56	—	—	—	9 ^e
Scrubber	8.0×10^9	0.02 ^d	107	—	—	—	>100% ^f
Activated alumina	6.2×10^{10}	77	—	—	—	—	23 ^g
Three process traps ^h	6.5×10^{10}	82.5	0.8	3.8	0.05	0.03	12.9 ^e

^a Remainder is largely due to $^{144}\text{Ce-Pr}$.

^b No other activity found by gamma spectrometric analysis.

^c Some $^{144}\text{Ce-Pr}$ also present (gamma spec).

^d One run only.

^e Trace amounts of $^{95}\text{Zr-Nb}$ also present (gamma spec).

^f Only ^{125}Sb detected (gamma spec).

^g Only ^{106}Ru detected (gamma spec).

^h Combined activity in process traps downstream of 400°C NaF trap for run SCAX-1; traps included 100°C NaF, 25°C NaF, and activated alumina.

TABLE II-31. DISTRIBUTION OF URANIUM AND FISSION PRODUCTS FOLLOWING FLUID-BED VOLATILITY PROCESSING OF IRRADIATED UO_2 —RUN SCAX-3

Reactor Charge

Irradiated Zircaloy-clad UO_2 containing 40 g UO_2 ; 2×10^{22} nvt; cooled 3 yr, $\gamma = 8 \times 10^{12}$ c/m, $\beta = 5 \times 10^{12}$ c/m, $\sim 5 \times 10^{13}$ d/m; 700 g granular alumina, 14-100 mesh

Process Conditions

HCl (Decladding) Step: $1\frac{1}{2}$ hr; Reactor 405°C ; Filter 350°C ; 50 v/o HCl in N_2

O_2 Step: 4 hr; Reactor 450°C ; Filter 440°C ; 20 v/o O_2 in N_2

F_2 Step: $14\frac{1}{2}$ hr; Reactor 450 – 550°C ; Filter 450 – 550°C ; 10-83 v/o F_2 in N_2

Percent of Charge

^a Identified as being the major gamma activities by gamma spectrographic analyses.

(1) Distribution of Uranium and Fission Products

The distribution of uranium and fission products in the process equipment during the various process steps of run SCAV-1 is shown in Table II-33.

1. *Uranium*. The uranium was collected primarily in the NaF trap maintained at 150°C . About 7% of the uranium was also found in the cold trap downstream of the NaF traps, indicating loss of uranium through the NaF bed at 150°C . Only a trivial amount of uranium (less than 0.1% of the charge) remained in the reactor and filter beds following fluorination.

2. *Cerium*. Since cerium forms a fluoride of very low volatility, the expected behavior of cerium was observed—cerium was found almost entirely in the reactor and filter beds. Considerable entrainment of cerium as a particulate material occurred; 13% of the amount charged collected on the packed-bed filter.

3. *Cesium*. The bulk of the cesium was found in the reactor and filter beds. The cesium analyses were uniformly low owing to volatilization of cesium from the bed sample during fusion of the sample at 1000°C with sodium borate-sodium carbonate. An alternative analytical method which avoids the fusion step is under development. The substantial accumulation of cesium in the 150°C NaF trap (0.51%) indicates the

TABLE II-32. DISTRIBUTION OF PLUTONIUM AND GAMMA ACTIVITY IN THE EXPERIMENTAL UNIT FOLLOWING PROCESSING OF IRRADIATED AND NONIRRADIATED UO_2 - PuO_2 FUEL

Sample	Run SCIV-2 (nonirradiated charge)		Run SCAV-1 (5300 Mwd/ton)	
	Pu (w/o)	γ (c/m)	Pu (w/o)	γ (c/m)
Charge		~ 0		6×10^{12}
Reactor bed	0.002 ^a	5.4×10^{10}	0.007 ^b	6.4×10^{11}
Filter bed	0.002 ^a	9.5×10^{10}	0.003 ^b	7.5×10^{11}
Condenser		1.6×10^{11}		3×10^{10}
Scrubber		1.3×10^{10}		5×10^9
Nickel balls		1×10^{10}		2.8×10^{10}
NaF, 150°C		9×10^9		5.8×10^{10}
NaF, 400°C		6×10^9		1.7×10^{11}
Cold trap		1.3×10^9		3×10^{11}
Activated alumina		9×10^7		7×10^{10}

^a These values calculated from a measured specific activity $\text{Pu} = 2 \times 10^8$ d/mg.

^b These values calculated from a calculated specific activity $\text{Pu} = 3 \times 10^8$ d/mg.

need for additional improvement in filtration, such as that afforded by sintered metal filters.

4. *Ruthenium*. The major fraction of the ruthenium

TABLE II-33. DISTRIBUTION OF URANIUM AND FISSION PRODUCTS FOLLOWING FLUID-BED VOLATILITY PROCESSING OF IRRADIATED $\text{UO}_2\text{-PuO}_2$ —RUN SCAV-1

Reactor Charge

Irradiated Zircaloy-clad $\text{UO}_2\text{-1}\frac{1}{2}$ w/o PuO_2 containing 173 g oxide, 5300 Mwd/t, cooled 22 months, $\gamma = 6 \times 10^{12}$ c/m, $\beta = 6.5 \times 10^{12}$ c/m, $\sim 6.5 \times 10^{13}$ d/m; 700 g granular alumina, 12–100 mesh

Process Conditions

HCl Step: 3 hr; Reactor 415–460°C; Filter 395°C; 50–70 v/o HCl in N_2

O_2/F_2 Step: $3\frac{1}{4}$ hr; Reactor 465°C; Filter 455°C; 25 v/o O_2 , 6 v/o F_2 , 69 v/o N_2

F_2 Step: 20 hr, Reactor 450–550°C; Filter 450–550°C; 7–90 v/o F_2 in N_2

Percent of Charge

^a These values probably were substantially influenced by residual activity in the equipment from previous hot runs.

^b A combined analysis for the two beds was performed which resulted in a total U content of 0.09% of the charge.

^c Analysis known to be low. New analysis under development.

was volatilized from the reactor during fluorination. The volatile fraction distributed throughout the various traps, as shown in Table II-33. Sodium fluoride at 400°C was considerably more efficient for ruthenium collection than NaF at 150°C. It should be noted that although a large fraction of ruthenium was condensed in the cold traps, about 3% of the amount charged passed through the traps and was collected on the activated alumina trap. As described in greater detail in the following paragraphs, a small amount, about 2.2 mCi or about 0.03% of that charged, passed out through

the activated alumina trap and was discharged to the environment through the cave stacks.

(2) Ruthenium Activity in the Cave Stack Gas

Prior to run SCAV-1, only trace amounts of ruthenium activity were found in the stack discharge by beta monitoring and stack gas sampling using activated charcoal cartridges. During run SCAV-1, the counting rate for the stack effluent rose rapidly from a normal background rate of about 200 c/m to 16,000 c/m after about 7 hr of fluorination. The run was in-

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FIG. II-26. Ruthenium Concentration in the Stack Gas during Run SCAV-1. (Total flowrate: Tests 1, 2, 4, 5, 6, 7: 3 liters/min; Test 3: 4 liters/min.)

interrupted at this point and an examination of the stack probe showed that deposited activity on the probe gave a reading of about 1 mr/hr at 1 inch. A gamma spectrometric analysis showed that the activity deposited on the probe was ^{106}Ru . The stack gas samples were counted for both ^{106}Ru and ^{125m}Te and the results were compared to a known standard to estimate the quantities of each isotope. The results showed that the concentration of ^{106}Ru was about $7 \times 10^{-8} \mu\text{Ci/cc}$ in the gas exhausting from the cave and that the calculated ground concentration was $3.6 \times 10^{-9} \mu\text{Ci/cc}$ (to transform concentration in samples taken at the sampling port to concentration at ground level, a dilution factor of 20 is applied). The calculated ground concentration was therefore 60% of the value recommended as an upper limit in the Radioactivity Concentrations Guide (RCG).⁷¹ Based on the measured concentration of ^{125m}Te in the stack gas, the concentration of ^{125m}Te at ground level was calculated to be $1.3 \times 10^{-11} \mu\text{Ci/cc}$, or $1.3 \times 10^{-2}\%$ of the RCG limit.

A series of short tests were performed in which a variety of solid sorbents and scrub solutions were evaluated to determine their effect upon ruthenium removal from the effluent process gas. The results of

this series of tests are shown on Figure II-26. The addition of an activated alumina trap temporarily decreased the ^{106}Ru level in the stack gas (tests 1 and 2); however, the concentration of ruthenium in the off-gas was high in a test in which a new activated alumina trap in series with a small absolute filter was used (test 4). Caustic scrubbing (test 5) with a 6M solution of NaOH did not reduce the ruthenium level nor did replacing the caustic scrubber with an activated charcoal trap at room temperature (test 6). A significant reduction in ruthenium concentrations in the stack gas was achieved when the 400°C NaF trap was emptied of NaF pellets and charged with a new batch of pellets. The reduction in ruthenium concentration achieved was sufficient to permit the run to be completed.

The efficiency of the BPL charcoal⁷² sampling cartridges used to determine stack concentration of ruthenium was determined by placing two sample cartridges in series during each of two sampling runs and analyzing each cartridge separately. The second cartridge in each of two tests showed no activity. The activity levels were such that the efficiency of charcoal for these two tests was greater than 90%.

An additional test was made to determine the physi-

⁷¹ AEC Manual, Chapter 0524, Standards for Radiation Protection (Approved Aug. 12, 1963).

⁷² A product of the Pittsburgh Chemical Co., 12-30 mesh

Ruthenium Activity Deposition

Route 1		Route 2	
Sample	Activity (mCi)	Sample	Activity (mCi)
Housing A	6.8×10^{-6}	BPL-2	9.5×10^{-5}
Filter Disc	4×10^{-5}		
Stainless Steel Disc	1.4×10^{-5}		
Housing B	1.9×10^{-6}		
BPL-1	2.4×10^{-5}		
	8.7×10^{-5}		

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FIG. II-27. Test for Ruthenium Particulate

cal state of the ruthenium activity, i.e., whether ruthenium was present as a particulate solid or gaseous species. In this test samples were taken from parallel streams. One of the streams passed through a filter cartridge containing a sheet of MSA 1106B filter paper⁷³ followed by a backup BPL charcoal cartridge. The other stream passed through a trap containing a BPL charcoal cartridge. The results of the analysis are

shown in Figure II-27. The activity picked up by the filter paper was equivalent to 42% of the activity deposited in all the components in Route 1 (Fig. II-27). The deposition of ruthenium activity on the stack probe and on metal surfaces adjacent to the probe suggests that some or all of the fraction found on the filter paper may be the result of gas-solid reaction. Similarly, this behavior suggests that the ruthenium is primarily present as a gas.

The total amount of ^{106}Ru discharged through the stack for the entire series of tests and during run SCAV-1 was 2.2 mCi, which represents about 0.03% of the ^{106}Ru initially charged to the reactor.

(3) Plutonium Removal from the Reactor and Filter Beds

As previously noted, runs SCIV-2 and SCAV-1 were made using $\text{UO}_2\text{-PuO}_2$ feed materials prepared from the same batch under similar processing conditions. The comparison of plutonium distribution throughout the process equipment (Table II-32) shows that the use of an irradiated charge resulted in an increase in plutonium retention in the reactor bed of 0.007 w/o compared to 0.002 w/o. This result tends to confirm laboratory results for nonirradiated charges with fission element additions in which the addition of cesium was shown to result in greater plutonium retention. It should be noted, however, that other studies have shown that these fluorination conditions are not optimum and that further removals of plutonium from the reactor bed would be possible by lowering the initial fluorination temperature (see section II.A. of this report).

5. Disposal of Gaseous Fluoride Volatility Reagents (J. T. HOLMES, C. B. SCHOFFSTOLL)

A bench-scale fluidized-bed facility is being used to study the reactions of gaseous fluoride volatility reagents with various reactive solids as a means of disposal of the gaseous reagents. The use of a fluidized bed of reactive solids was chosen for the following reasons:

a) Owing to the good heat transfer achieved in fluidized beds, it is possible to carry out highly exothermic gas-solid reactions under nearly isothermal conditions and thereby prevent sintering, which often occurs in packed-bed reactors.

b) The reactive solids can be chosen such that the products of the reaction are solids and nontoxic gases. A solid product is important for ultimate waste disposal if the gaseous reagents contain volatile fission product compounds which also react with the solids.

Initial work is being specifically devoted to the disposal of fluorine, using fluidized beds of activated alumina. The work will be extended to evaluate the use of other solids such as lime, limestone, and soda ash for fluorine disposal and then, using appropriate solids, to the disposal of other gaseous reagents such as the bromine fluorides, ClF_3 , HF , HCl and possibly fission product compounds.

A bench-scale fluidized bed apparatus has been constructed and a series of shakedown runs have been completed on the reaction of fluorine with activated alumina (Alcoa grade F-1). The results of the shakedown runs indicated that the reaction was highly efficient (as high as 99.99%) in removing fluorine from a gas stream. The capacity of the activated alumina for fluorine was as high as 0.7 g F_2/g activated alumina.

⁷³ A product of Mine Safety Appliances.

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FIG. II-28. Equipment for Studying the Disposal of Gaseous Reagents from Fluoride Volatility Processes.

a. EQUIPMENT

The bench-scale apparatus for these studies is shown schematically in Figure II-28. The 24-in. long fluidized-bed reactor is a 2-in. dia. schedule 40 nickel pipe with a 60° cone bottom. A sintered alumina ball rests in the cone and prevents solids from leaving the reactor. A 3-in. dia. disengaging section is connected to the fluid bed by a 60° conical section. The disengaging section contains two, 9-in. long, bayonet-type filters of sintered nickel. The filters are equipped with an automatic blow-back device for periodic return of fine particles from the filters to the bed.

The gaseous inputs are metered with orifices and are regulated by automatic control valves. The total flow rate is maintained at a constant value by providing nitrogen diluent. The fluid-bed section of the column is heated by three 1000-watt tubular heaters. Each heater is controlled by a proportioning type controller which senses a thermocouple on the wall of the column near the heater. Water is supplied to a cooling coil which encompasses the entire length of the fluid-bed section. The coolant controller senses three thermocouples which are located at 1-in. intervals in the fluidized bed. The lowest thermocouple is located at the top of the cone inlet. These thermocouples are connected in

parallel so that they give the "average" temperature of the reaction zone.

Two gas analyzers are being used to monitor the off-gas from the fluid-bed reactor. A thermal conductivity cell is used to continuously measure high fluorine concentrations (>1000 ppm). A small scrubber containing potassium iodide solution is used intermittently to measure low fluorine concentrations (<1000 ppm).

The thermal conductivity cell is a glass-bead thermistor type. The fluorine gas stream passes through the reference side of the cell. The sensitivity of the unit to fluorine is increased by converting the fluorine to chlorine (using a bed of NaCl) prior to passing the gas through the sample side of the cell. The cell is thermostated at about 15°C. The sensitivity of the cell is 1000 ppm/mv over the range 0–10,000 ppm. There does not appear to be any significant corrosion of the glass bead thermistors owing to contact with fluorine at concentrations up to 10,000 ppm.

The scrubber for measuring low fluorine concentrations consists of a 3-in. dia. glass pipe, 24 in. long, with the lower 12 in. packed with 4- to 5-mm dia. glass beads. A sample of the off-gas from the fluid-bed reactor is bubbled through 1.0 liter of 0.1M potassium io-

ide solution. The fluorine oxidizes the iodide ion to iodine which remains in solution. The iodine concentration is measured by titrating a sample with a standard sodium thiosulfate solution. The sensitivity of the scrubber and titration technique is 84 ppm/min, tested over the range 6 to 2600 ppm. This means that, if the scrubber samples the reactor off-gas for a period of 10 min, the minimum fluorine concentration which can be detected is 8.4 ppm over the 10-min period. It is planned to replace the scrubber with a photometric gas analyzer for continuously monitoring the reactor off-gas for low concentrations of fluorine.

b. EXPERIMENTAL PROGRAM

An experimental program has been designed to study the reaction of fluorine with activated alumina. The purpose of the program is to determine the effects of the significant system variables on the efficiency of fluorine removal from the gas stream and on the extent of reaction of the fluid-bed solid. The efficiency of removal will be used to predict the magnitude of environmental contamination problems and to determine if multiple-stage reactors or back-up trapping schemes are needed. The extent of reaction of the fluid-bed solid material will be used to determine the total amount of solid reagent required and allow estimation of the economics of the processing technique.

It is thought that temperature, fluorine concentration, ratio of bed height to diameter, gas velocity, and fluid-bed particle size are the independent variables which have the greatest effect on the efficiency of fluorine removal and on the extent of reaction of the solids. To study the effects of these five variables and all possible interactions of the variables, a factorial design involving $(2)^5$ experiments would be needed if each variable were investigated at a high and a low value. Since this number of experiments (32) may be impractical to perform for each gas-solid system of interest, a fractional factorial design will be used wherein only 8 ($1/4$ replicate) or 16 ($1/2$ replicate) experiments are used to determine the effect of all of the independent variables and some of the interactions. A one-half replicate experiment will be used on the reaction of fluorine with activated alumina. When the effects of the five variables are determined, optimization techniques may be used to indicate where a few additional experiments should be made in search of an optimum set of conditions for each gas-solid system. Concurrent with the determination of an optimum set of conditions, kinetic models will be tested using the data from the fractional factorial experiments.

. RESULTS AND DISCUSSION

Ten shakedown runs have been made to establish the levels of the independent variables to be used in the

factorial design for the reaction of fluorine with activated alumina and to gain experience with operating the new apparatus. Four runs were made with 50 v/o fluorine in nitrogen and a total flow rate sufficient to give about 1.5 times the minimum fluidization velocity measured at the reaction temperature. Six runs were made with 10 v/o fluorine in nitrogen at about 1.2 times the minimum fluidization velocity measured at room temperature. The reaction temperatures for this series of runs ranged from 100 to 500°C.

The following observations were made from the shakedown runs:

1. *Nature of the Reaction.* In all of the runs, most of the reaction occurred near the gas inlet at the bottom of the reactor. In the runs using high fluorine concentrations (50 v/o) and low superficial velocities, axial temperature gradients of up to 250°C were observed over an 8-in. interval in the bed. Since these large gradients prevent an accurate definition of the reaction temperature, the fluorine concentration was reduced (10 v/o) and the superficial velocity increased. This procedure was successful in reducing the gradients to less than 50°C. The concentration of fluorine in the off-gas from the reactor varied as a function of time. At the outset of the run, the concentration remained below 10 ppm, and this level was maintained for about 20 to 40% of the total run time. The concentration then gradually increased, usually to less than 200 ppm, over the remaining 80% of the run time until breakthrough was noted. Breakthrough was characterized by a rapid increase in the fluorine concentration to over 1000 ppm, and a decrease in the temperature of the lower portion of the fluidized bed. The fluorine input was stopped at the time the breakthrough was observed.

2. *Efficiency of the Reaction.* The efficiency of removal of fluorine was over 99.99% during the initial part of the run, and over 99.9% for the remainder of the run prior to the breakthrough. The capacity of the activated alumina was as high as 0.7 g F_2 /g activated alumina.

3. *Operating Results.* The runs were performed without difficulties. The automatic blow-back device was not needed to clean the filters during any of the runs. There was no evidence of significant attrition of the bed particles or of sintering or caking of the bed.

d. CONCLUSIONS

The use of fluidized beds of reactive solids provides a promising method for the disposal of gaseous fluoride volatility reagents. The reaction of fluorine with activated alumina is highly efficient with respect to (1) fluorine removal and (2) the capacity of the activated alumina. The product of the reaction is a solid, which is desirable from a waste disposal standpoint.

e. FUTURE WORK

The effect of temperature, fluorine concentration, superficial gas velocity, particle size of the fluid-bed solid, and bed depth will be determined for the reaction of fluorine with activated alumina, using a factorially designed set of experiments. The temperature levels will be 300 and 400°C; the fluorine concentrations, 5

and 10 v/o; the superficial gas velocities, 1.2 and 1.5 times the minimum fluidizing velocity measured at room temperature; the particle sizes of activated alumina, 28-48 mesh and 48-100 mesh; and the bed depth to diameter ratios will be 3 and 6.

Other solids such as lime, limestone, and soda ash will then be evaluated for fluorine disposal.

C. BASIC STUDIES OF FLUIDIZED-BED BEHAVIOR RELATED TO PROCESS OPERATIONS (D. RAMASWAMI)

1. Basic Mechanisms of Fluidization (J. D. GABOR, R. E. CARLSON⁷⁴)

The characteristics of particle movement at the walls of a fluidized bed are important for control of fluid-bed reactor systems. For most reactor systems, heat is either introduced or removed through wall surfaces. The presence of walls also affects the characteristics of gas and particle mixing within the reactor. Therefore, knowledge of particle behavior, particularly in the vicinity of reactor walls, is of practical importance to the design of fluid-bed systems.

The analysis of particle movement and gas flow in fluidized beds from principles of theoretical fluid dynamics has been shown to give an adequate description of these processes. Davidson⁷⁵ predicted the gaseous cloud about the rising bubbles in a fluidized bed. Rowe⁷⁶ has shown a correspondence of particle movement in a fluidized bed, caused by the rising bubbles, to the drift of ideal fluid elements in an infinite medium. In this analysis, Rowe considered that the drift of the fluid elements was induced by the passage of a solid cylinder, as suggested previously by Darwin.⁷⁷ Collins⁷⁸ extended Davidson's theory for two-dimensional fluidization to the case for a bubble midway between the walls of the column.

Current work involves an extension of the previous fluid-dynamic principles to include the effect of walls on particle movement and on transport processes.

a. MODEL FOR WALL EFFECTS ON PARTICLE MOVEMENT

The prior theoretical and experimental research has shown that a strong resemblance exists between the

motion of a fluidized particle induced by rising bubbles and the hypothetical motion of an ideal fluid around the bubble. An ideal fluid is one which is incompressible and has negligible viscosity. This resemblance is of considerable practical significance for studies of complex transport or reaction phenomena in fluidized beds for two major reasons:

- 1) Almost all significant particle mixing which occurs during fluidization is caused by bubbles; and
- 2) Fluid mechanics theory is well developed for ideal fluids, and often permits relatively easy calculation of the fluid motion.

If one considers a two-dimensional fluidized bed, i.e., a bed of rectangular cross section for which the thickness is so small that a rising bubble is in simultaneous contact with both opposite walls (and therefore appears as a "hole" in the bed), then to a crude approximation the bubble is circular and the particle motions may be calculated from the flow of an ideal fluid past a circular cylinder. Theoretical flows of ideal fluids may be represented by stream functions. Again, in two dimensions, the usual coordinate system of x and y may be considered. The stream function $\psi(x,y)$ has the property that lines of constant ψ (loci of points x,y such that ψ takes on a particular, constant value) correspond to flow paths of the fluid. The flow problem is solved once a ψ is found to match the system boundaries. For uniform flow normal to a row of equally spaced, approximately circular bubbles (which corresponds to a bubble midway in a channel of parallel walls), the stream function, ψ , is:

$$\psi = U_B \left[y - a \tan \frac{\pi a}{2d} \left(\frac{\sin \frac{\pi y}{d}}{\cosh \frac{\pi x}{d} - \cos \frac{\pi y}{d}} \right) \right] \quad (1)$$

where

a = bubble radius

⁷⁴ Co-op student from Northwestern University.

⁷⁵ Davidson, J. F. and Harrison, D., "Fluidized Particles," Cambridge University Press, Cambridge, 1963.

⁷⁶ Rowe, P. N., Chem. Eng. Progr. Symp. Ser., **58**(38), 42-56 (1962).

⁷⁷ Darwin, Charles, Proc. Cambridge Phil. Soc., **49**, 342 (1953).

⁷⁸ Collins, R., Chem. Eng. Sci., **20**, 747 (1965).

FIG. II-29. Particle Drift for $a/d = 0.5$.

$d = 1/2$ distance between the parallel walls

U_B = bubble velocity.

The particle velocity in the x direction can be determined by differentiating the stream function with respect to y .

$$\frac{dx}{dt} = \frac{\partial \psi}{\partial y} = U_B \left\{ 1 - \frac{\pi a}{d} \tan \frac{\pi a}{2d} \left[\frac{\left(\cosh \frac{\pi x}{d} - \cos \frac{\pi y}{d} \right) \cos \frac{\pi y}{d} - \sin^2 \frac{\pi y}{d}}{\left(\cosh \frac{\pi x}{d} - \cos \frac{\pi y}{d} \right)^2} \right] \right\} \quad (2)$$

where t = time.

The total displacement, x , by a particle as a bubble passes is found by integrating over a constant ψ (between limits of $t = -\infty$ to $t = +\infty$) the difference between the velocity of the passing bubble and the velocity of the fluid in the x direction.

$$x = \int_{-\infty}^{\infty} \left(U_B - \frac{dx}{dt} \right) dt \quad (3)$$

The above integration is facilitated by transformation to polar coordinates of r and θ .

$$x = \int_0^\pi \left(U_B - \frac{dx}{dt} \right) \left(r / \frac{\partial \psi}{\partial r} \right) d\theta \quad (4)$$

The integral in Eq. 4 was solved numerically⁷⁹ using the trapezoidal rule for $\theta = 0.01, 0.02, 0.03, 0.04, 0.05, 0.10, 0.15, \dots, 0.55$, and $\pi/2$.

Figure II-29 described the particle movement for an a/d ratio of 0.5. The particles near the wall move downward as the bubble passes. The two-dimensional system portrayed in the figure is analogous to taking a thin vertical slice of a cylindrical, three-dimensional column where the edges would correspond to the walls of the column. The particles in the center move forward and then loop with a resultant net forward displacement. This behavior is characteristic of particle circulation in fluidized beds. The particle movement is generally upward in the center of the bed and downward at the column walls.

Also shown in Figure II-29 are the positions of the particles in relation to the time during the passage of the bubbles. Zero time is taken as the instant when the center of the bubble is at 0 on the x coordinate. The times at any position, based on a bubble velocity of 1 (note $d = 1$), are given in terms of the relative dis-

⁷⁹ Program B-189 (3600F), Argonne National Laboratory Applied Mathematics Program Library.

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FIG. II-30. Total Particle Drift Caused by Bubble Rising Between Parallel Walls at $a/d = 0, 0.05, 0.1, 0.3, 0.8$, and 0.95 .

placement of the bubble. Therefore, at $t = \frac{1}{4}$ the bubble has moved $\frac{1}{4}$ of a bubble diameter from time 0.

Final particle displacements caused by the passage of a bubble rising from minus infinity to plus infinity are depicted in Figure II-30. The final displacements are shown at several levels of the parameter a/d between 0 (for case of no walls, in which Darwin's solution was used) and 0.95. The curves are based on a bubble diameter equal to 1. The line $x = 0$ represents the original position of the particles before passage by the bubble, and the ends of the lines are terminated at the wall except for the cases of $a/d = 0.05$ (where the

walls are at $y = \pm 10$) and $a/d = 0$ (where there are no walls).

b. FUTURE WORK

Future work will be primarily experimental. A two-dimensional column of variable width will be constructed. The column will include a device for injection of single bubbles. High-speed motion picture photography will be used to assist in the comparison of actual fluidized particle movement with that described by theory.

2. Mechanism of Heat Transfer Between Wall and Bed (L. B. KOPPEL,⁵⁴ J. T. HOLMES, R. D. PATEL⁸⁰)

Despite considerable recent research on heat transfer in a fluidized bed, the process is not yet well understood. A model⁸¹ was previously proposed relating the bed-to-wall heat transfer coefficient to the residence time of the fluidized particles at the wall. To verify this model, an experimental program has been estab-

lished and construction of equipment has been initiated.

The main feature of the new equipment is that particle residence times and heat transfer coefficients can be measured at an identical surface under identical fluidization conditions. This is the first known attempt to make such measurements.

The apparatus consists of a 4-in. dia. stainless steel pipe, with a 2½-in. wide Lucite plate mounted in a

⁸⁰ Graduate student from Purdue University.

⁸¹ Ziegler, E. N., Koppel, L. B., and Brazelton, W. T., *Ind. Eng. Chem. Fundamentals*, **3**, 325 (1964).

slot cut in the pipe along its entire length. The steel pipe serves as the fluid-bed column. The Lucite plate is interrupted 5 in. above the distributor plate by a rectangular cavity, 4 in. high and 2½ in. wide. This cavity serves to accommodate the heating surface or the photographic window. Provision has been made for mechanical stirring of the bed, should this prove necessary to achieve good solids mixing.

The heating surface is a copper block (surface measurements 2 in. by 1½ in.) mounted in a larger Lucite block, which is machined to fit the cavity in the fluid-bed column. A 10-watt electrical heating element is mounted behind the copper block. The d-c power supply to this element is metered by a voltmeter-ammeter combination. Five thermocouples are mounted near the surface of the copper block to measure the surface temperature. The temperature of the bed is also measured at certain positions. Fluidizing air is metered

through a rotameter, and introduced to the bed through a sintered bronze distributor plate.

The photographic window is an optically clear Lucite block. A fraction of the fluidized particles are suitably colored to serve as tracers. The particles at the window are repeatedly photographed and particle residence times at the surface are calculated from tracer particle counts of the film by employing the statistical techniques described in ANL-7125, pp. 105-106.

Heat transfer measurements will be made with the heater block in the cavity. After these measurements are completed, the heater will be removed, the photographic block inserted, and the surface photographed at the same bed conditions to determine particle residence times. The measured heat transfer coefficients and corresponding particle residence times will be used to evaluate existing theories of fluidized-bed heat transfer.

III

Materials Chemistry and Thermodynamics¹

A. HIGH TEMPERATURE MATERIALS DEVELOPMENT

(R. K. EDWARDS, H. M. FEDER, M. ADER)

This program is directed toward the development of nuclear reactor materials that will be subjected to high temperatures (1500 to 3000°C). Its objective is to collect basic data on the vaporization and chemical stability of potential fuels, i.e., the oxides, carbides, nitrides, phosphides, sulfides, and arsenides of uranium, plutonium, and thorium, and their solid solutions; and on the reactions of these materials with other substances. The collected data will be useful for guidance in materials selection; it will also serve to advance knowledge of non-stoichiometry in solids, an important high-temperature phenomenon. Experimentation is carried out quantitatively so as to yield thermodynamic and phase-diagram information. Various complementary methods of investigation are used,

according to the requirements of the particular problem.

During the past year, emphasis has been placed on determinations of the phase diagram of the condensed uranium-urania² system, the equilibria between the vapor and condensed phases of this system, and the oxidation-reduction equilibria of urania. The specific objective of these studies was to obtain comprehensive thermodynamic data for compositions ranging from nearly pure uranium to slightly hyperstoichiometric urania. Some exploratory work to evaluate the effect of tungsten on the uranium-urania system was also carried out. A survey and an evaluation of the pertinent literature on the urania-plutonia and uranium carbide-plutonium carbide systems have been initiated preparatory to experimental studies of these systems.

1. Condensed Phase Studies (A. E. MARTIN, F. C. MRAZEK)

a. THE URANIUM-URANIA SYSTEM

Final evaluation of our phase-diagram data³ for the uranium-urania system is being made and a manuscript is being prepared for journal publication. The experiments performed during the current report period were directed toward clarification of questions arising from this evaluation.

The only modification that was made of the phase diagram previously presented is a minor refinement of the monotectic composition, now indicated as $1.33 \pm$

0.03 rather than 1.30 ± 0.10 O/U atom ratio units. The new value resulted from the chemical analysis of the oxide portion of a particularly well-melted arc preparation having a composition in the miscibility gap region of the diagram.

The hypostoichiometric boundary of the urania phase was previously established by the oxide-growth technique⁴ for temperatures ranging between 2470°C, the monotectic temperature, and 1590°C. However, the lowest temperature at which a substantial oxide growth was obtained was 1815°C. Hence, the boundary was relatively poorly defined below this temperature. In an attempt to improve this situation, two oxide-growth experiments were carried out at 1350 and 1450°C for 261 and 168 hr, respectively. These experiments employed crucibles made from single crystals of uranium dioxide (supplied through the courtesy of H. J. Ander

¹ A summary of this section is given on pages 11 to 14.

² The term urania will be used in Section IIIA to denote a solid phase, of fluorite structure, with unspecified composition; the symbol UO_2 will be used to denote stoichiometric uranium dioxide. The terms hypostoichiometric and hyperstoichiometric refer to the oxygen in urania; the symbols UO_{2-x} and UO_{2+x} denote hypostoichiometric and hyperstoichiometric urania, respectively.

³ ANL-7125, pp. 119-120.

⁴ ANL-7020, p. 61; ANL-6925, p. 171.

on of Pacific Northwest Laboratory) instead of the usual polycrystalline crucibles. As anticipated from prior work at low temperatures, the oxide growths obtained were insufficient for useful analysis. However, because these crucibles were free of porosity, it was thought that their compositions might be equivalent to those of oxide growths formed at the same temperatures. The O/U ratios of the crucibles were found to be 1.958 and 1.946 at 1350 and 1450°C, respectively, and were more hypostoichiometric by about 0.03 units than the ratios obtained by extrapolating the previously obtained oxide-growth data to these temperatures. Although there is some question as to how accurately these analyses define the hypostoichiometric boundary, the data do constitute further evidence for the absence of intermediate phases between uranium and urania above 1350°C.

b. THE URANIUM-URANIA-TUNGSTEN SYSTEM

The study of the ternary uranium-urania-tungsten system was initiated⁵ because of its relevance to the suggested use of tungsten as a cladding for high-temperature urania fuels, and because tungsten has been used as a container material in much of the experimentation on uranium-urania systems. The study has been exploratory in nature and primarily intended to permit assessment of the need for a more detailed study.

The general form reported⁶ for the binary W-U system, namely, that of a simple eutectic system, was confirmed. The binary W-UO₂ system appears to be the same type, with the eutectic close to the composition UO₂. The liquid miscibility gap found to exist in the uranium-urania system above 2470°C extends into the ternary system. The distribution of tungsten between the two immiscible liquids strongly favors the metallic phase.

Further study of this ternary system is not planned in view of the very limited solubility of tungsten in urania.⁵

c. HIGH-TEMPERATURE THERMAL ANALYSIS APPARATUS

A thermal analysis apparatus is being developed to facilitate the study of phase diagrams at high temperatures. A Varian tungsten-resistance furnace capable of reaching 3000°C is being utilized. A Leeds and Northrup recording optical pyrometer will be used to record temperatures. The temperature of the furnace will be programmed during heating and cooling by mechanically driving a ten-turn potentiometer. The potentiometer controls the current to a saturable reactor that regulates the furnace temperature. For regular thermal analysis, TA, the temperature will be recorded versus time. For the detection of relatively small heat effects, this method will be supplemented by differential thermal analysis, DTA.

The recording optical pyrometer and some of the components of the temperature programmer have not yet been received. However, exploratory tests with the incomplete TA apparatus indicated that it was sufficiently sensitive to detect liquidus points up to the maximum operating temperature of the furnace.

The DTA equipment has been tested successfully to over 2700°C utilizing a W/W26% Re differential thermocouple to indicate thermal arrests and an optical pyrometer to measure the arrest temperatures. The DTA equipment is more sensitive than the TA arrangement and hence will be particularly useful in detecting small heat effects; e.g., it was sensitive enough to disclose the initial precipitation of liquid uranium at the hypostoichiometric urania boundary during the cooling of urania having an O/U ratio of 1.70.

2. Vaporization Studies

a. MASS-SPECTROMETRIC EFFUSION STUDIES IN THE URANIUM-URANIA TWO-PHASE SYSTEM (J. W. REISHUS, G. E. GUNDERSEN)

The Knudsen effusion method was used by Ackermann, Rauh, and Chandrasekharaiah⁷ (ARC) to determine the total pressure of uranium-bearing species over

the condensed two-phase system, uranium (*l*, sat'd with UO_{2-x}) in equilibrium with UO_{2-x} (*s*, sat'd with U). Their results for the range 1300 to 2000°C were expressed by

$\log P$ (atm)

$$= (7.25 \pm 0.14) - (27,024 \pm 255)/T. \quad (1)$$

They also obtained mass spectrometric data which, when coupled to Eq. 1, led to the following partial pressure equations:

$$\log P_U \text{ (atm)} = (5.194 \pm 0.140) - (25,620 \pm 300)/T; \quad (2)$$

⁵ ANL-7125, p. 120.

⁶ C. H. Schramm, P. Gordon, and A. R. Kaufman, *Trans. AIME* **188**, 195 (1950).

⁷ This work was carried out with interdivisional collaboration and is described in "A Thermodynamic Study of the Urania-Uranium System," by R. J. Ackermann, E. G. Rauh, and M. S. Chandrasekharaiah, ANL-7048, July, 1965.

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FIG. III-1. Mass Spectroscopic Measurements of U(g) , UO(g) , and $\text{UO}_2\text{(g)}$ in Equilibrium with $\text{U(l)}\text{-UO}_{2-x}\text{(s)}$. (Series 2 and 3 normalized to series 1 at 2200°K ; normalizing factors 1.04 and 0.919, respectively.)

$$\log P_{\text{UO}} (\text{atm}) = (7.109 \pm 0.140) - (26,870 \pm 300)/T; \quad (3)$$

$$\log P_{\text{UO}_2} (\text{atm}) = (7.728 \pm 0.140) - (30,165 \pm 300)/T. \quad (4)$$

Independent measurements by the present authors (RG) were started at the same time, but they were delayed because of a temperature measurement problem.⁸ The problem was resolved and the results are now reported.

The experimental procedures and the Bendix TOF mass spectrometer were essentially the same as in the mass spectrometric portion of the ARC study. Tungsten effusion cells were loaded with a mixture which consisted, typically, of a 60- to 100-mg uranium bead resting on a 200- to 300-mg disc of sintered urania. The

samples were kept small to minimize the equilibration time. To achieve consistency in the ion current (I_i) values for U^+ , UO^+ , and UO_2^+ at a given temperature, 1 to 3 hr of equilibration time was required.

Three individual series of measurements, taken with slightly different instrumental conditions, are summarized in Figure III-1. To facilitate intercomparison, the $\log I_i T$ values for series 2 and 3 were normalized to those of series 1 at 2200°K , the approximate midpoint of the temperature range (~ 2000 to 2400°K). The equations for the curves shown in Figure III-1 follow:

$$\log I_{\text{U}} T = (-26,441 \pm 1076)/T + (13.2940 \pm 0.4774); \quad (5)$$

$$\log I_{\text{UO}} T = (-26,966 \pm 558)/T + (14.8353 \pm 0.2540); \quad (6)$$

⁸ ANL-7125, p. 123.

TABLE III-1. ENTHALPIES OF VOLATILIZATION FOR THE TWO-PHASE SYSTEM $U(\ell)$ - $UO_{2-x}(s)$.
In kcal/mole

	ARC Results	RG Results
$\Delta H(U)$	117.2 ± 1.4	121.0 ± 4.9
$\Delta H(UO)$	122.9 ± 1.4	123.4 ± 2.6
$\Delta H(UO_2)$	138.0 ± 1.4	138.9 ± 2.5

$$\log I_{UO_2}T = (-30,361 \pm 539)/T + (15.4677 \pm 0.2434). \quad (7)$$

Table III-1 compares the enthalpies of volatilization derived from the present study with those derived from Eq. 2, 3, and 4 of the ARC study. The two studies give overlapping results within their stated errors. Because of the somewhat smaller errors, it is concluded that the ARC equations provide the more satisfactory summary of the partial pressure relationships among the gaseous species.

b. DETERMINATION OF COMPOSITIONAL CHANGES BY MASS-SPECTROMETRIC EFFUSION STUDIES (J. W. REISHUS, G. E. GUNDERSEN)

In a previous report,⁹ thermodynamic arguments were used to develop equations relating the changing, relative partial pressures of two vapor species to the composition of a vaporizing binary solid phase of variable composition. For the solid phase UO_{2+x} (x may be negative), the equations in terms of the principal vapor species are

$$\left(\frac{\partial \ln P_{UO}}{\partial \ln P_{UO_2}} \right)_T = \frac{1+x}{x} \quad (8)$$

and

$$\left(\frac{\partial \ln P_{UO_3}}{\partial \ln P_{UO_2}} \right)_T = \frac{-1+x}{x}. \quad (9)$$

These equations are believed to be valid, except at extremely small values of x . It was also noted that a continuous record of the pressures of a pair¹⁰ of species would, in principle, permit evaluation of the changing composition of the condensed phase and thus lead to the determination of the individual pressures as a function of x . For a binary solid phase that shifts composition during effusion vaporization, a mass spectrometer is a convenient device for obtaining a continuous isothermal "traverse." Thus, a single isothermal traverse experiment could yield a complete curve of ion current, I_i , vs. x . To obtain such a curve would otherwise require

many individual experiments, since each set of data would have to be associated with a value of x determined for the residual solid by means of chemical analysis. The traverse technique, of course, requires that equilibrium prevails at all times between the gas and the condensed phase within the effusion cell.

Some traverse experiments with hypostoichiometric urania (wherein x has a negative value) have been carried out in the Bendix TOF mass spectrometer to assess the limitations of the method. Since the equation $I_iT = CP_i$, in which C is a constant, relates the ion current to the partial pressure for a given effusing species, then

$$\begin{aligned} \left(\frac{\partial \ln P_{UO}}{\partial \ln P_{UO_2}} \right)_T &= \left(\frac{\partial \ln I_{UO}}{\partial \ln I_{UO_2}} \right)_T \\ &= \left(\frac{\partial I_{UO}}{\partial I_{UO_2}} \cdot \frac{I_{UO_2}}{I_{UO}} \right)_T = \frac{1+x}{x}. \end{aligned} \quad (10)$$

It is evident that the accuracy and precision with which x may be determined from the slope of a plot of I_{UO} vs. I_{UO_2} will be limited by drifts and fluctuations in sample temperature and in the electronics of the mass spectrometer. In the experiments being reported, urania and a small amount of uranium metal were put into tungsten effusion cells and heated under vacuum. Thus, the initial compositions were those of the hypostoichiometric phase boundary. A plot of I_{UO} vs. I_{UO_2} at 2375°K is shown in Figure III-2. The polynomial equation best fitted to the data by least squares was:

$$I_{UO} = 5.275 - 23.026 I_{UO_2} + 25.228 I_{UO_2}^2. \quad (11)$$

From the slope obtained at the end of the experiment, when $I_{UO_2} = 0.40$ in arbitrary units, the composition of the solid residue was calculated to be 1.918 ± 0.025 O/U atom ratio units. By combustion analysis of the residue, a value of O/U = 1.903 ± 0.009 was obtained. In another traverse experiment at a lower temperature, 2343°K, the slope analysis led to a final O/U ratio of 1.918 ± 0.031 , to be compared with 1.910 ± 0.004 from the combustion analysis of the residue. The traverse results are therefore in agreement with the more standard method, but appear to be less precise.

The errors in composition derived from the slope analysis arise from fluctuations in the ion current intensities and represent the limit of precision of the present instrument. As mentioned above, these fluctuations can be caused by temperature and/or electronic variations during an experiment. Experience has shown, however, that when the spectrometer is operating properly, the electronics are quite steady, and variations in the electron energy and intensity of the ionizing electron beam are considerably less than 1%. Thus, it is felt that the main factor limiting the precision of the

⁹ ANL-6925, pp. 168-170.

¹⁰ The pair can not differ in degree of polymerization only.

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FIG. III-2. Variation of I_{UO} vs. I_{UO_2} during Traverse of Hypostoichiometric Region of Urania at 2375°K.

data was a temperature fluctuation of $\pm 3^\circ\text{C}$. A fluctuation of $\pm 3^\circ\text{C}$ would give rise to partial pressure variations for UO and UO_2 of 2% and 4%, respectively. (Ion current fluctuations of up to 2% for UO and up to 6% for UO_2 were observed in the experiments described in Part 2b, although the condensed two-phase urania-uranium system should be invariant if the temperature is truly held constant.) Calculations indicate that to achieve a precision of ± 0.005 in the O/U ratio of the solid phase at 2100°C , the temperature would have to be regulated to within $\pm 0.8^\circ\text{C}$. This is a very severe requirement for any known power regulator.

These experiments seem to have provided adequate "proof of principle" for the new technique. Despite the temperature-control limitation, this technique is likely to be useful in other high-temperature studies.

c. THE CONGRUENTLY VAPORIZING COMPOSITION OF URANIA (M. S. CHANDRASEKHARAIHAH, P. M. DANIELSON)

The previously reported survey¹¹ of the literature relating to the congruently vaporizing compositions of

urania revealed the necessity for the unambiguous establishment of these compositions as a function of temperature. Accordingly, experiments are being made in which approximately 50% of large samples of urania are vaporized from a Knudsen effusion cell into an ultrahigh vacuum. The compositions of the residues are determined by combustion analysis. Thus, the experiments are being conducted in a manner intended to keep the results free from the principal weaknesses of previous work, namely (1) insufficient amounts of sample vaporized, and (2) vacuum environments which might have buffered the urania at compositions which did not vaporize congruently.

A typical experiment was carried out in the following way. A urania sample (2 to 3 g) of known composition was put in a tungsten effusion crucible (knife-edge orifice, 0.040 in. in diameter), and the crucible was positioned within the furnace system. The system was first evacuated and then baked at 250°C until the residual pressure was reduced to 10^{-11} torr. Next, the crucible was brought slowly to the run temperature by induction heating. The heating was carried out in such a way that the residual pressure was generally kept

¹¹ ANL-7125, pp. 122-123.

below 10^{-8} torr. The crucible was maintained at the run temperature until one-third to one-half of the sample was vaporized. The composition of the residual gas was monitored throughout by means of a quadrupole mass spectrometer. The residual total pressure observed toward the end of a run was 10^{-10} torr; the residual partial pressure of oxygen was less than 10^{-12} torr. At these pressures the residual oxygen in the vacuum system can not buffer the composition of the urania sample because the rate of effusion of oxygen from the cell is two orders of magnitude higher than the rate of inleakage.

The results obtained so far are tabulated in Table III-2. It should be noted that the congruently effusing compositions were approached from both higher and lower initial O/U ratios, which indicates that constant compositions had been attained. The data, plotted as a function of temperature in Figure III-3, indicate a variation of the congruent composition with temperature. Runs 1, 2, and 3, whose initial compositions were relatively high in oxygen content, were not included in drawing the curve since insufficient time had been allowed to reach the congruently vaporizing composition for the temperatures (and crucible) used. (Evaporation of too much charge leaves a residue too small for accurate combustion analysis.)

These results confirm our previous suspicions¹¹ regarding the hypostoichiometric nature of congruently effusing urania. A few more confirmatory experiments are planned.

TABLE III-2. COMPOSITIONS OF CONGRUENTLY EFFUSING URANIA

Run	Temp. ($\pm 10^\circ\text{C}$)	Weight of Urania (g)		Composition, O/U Atom Ratio	
		Initial	Residual	Initial (± 0.01)	Residual (± 0.004)
11	2026	1.9	1.5	1.91	1.996
10	2140	1.9	1.2	1.90	1.985
1	2170	2.1	1.2	2.11	1.997
7	2200	2.3	1.4	1.92	1.970 ^a
9	2200	2.7	1.7	1.93	1.968, 1.974 ^b
3	2219	3.3	1.4	2.09	1.990
2	2225	2.0	1.1	2.09	1.981
8	2230	2.1	1.5	1.92	1.967
12	2245	1.9	0.9	1.90	1.962
4	2290	3.0	1.5	2.09	1.940
6	2290	3.6	2.2	1.89	1.945, 1.950 ^b

^a Tungsten contamination suspected from yellow color of residue after combustion for O/U analysis.

^b Two separate O/U analyses made on residue.

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FIG. III-3. Compositions of Congruently Effusing Urania. (Numbers at data points indicate run numbers.)

d. THE TOTAL VAPOR PRESSURE OF URANIUM-BEARING SPECIES AND THE PARTIAL PRESSURE OF OXYGEN OVER URANIA (M. TETENBAUM, P. D. HUNT)

Measurements of the total pressure of uranium-bearing species over urania by the transpiration method and the simultaneous determination of the partial pressures of oxygen have progressed¹² and additional isotherms can be presented. The measurements are conducted with $\text{H}_2\text{-H}_2\text{O}$ gas mixtures which serve, by equilibration, to fix the oxygen partial pressures and thereby to control the compositions of the solid phases. The accumulated data at temperatures ranging from 2080 to 2705°K are presented in Figures III-4 and III-5.

The isotherms given in Figure III-4 are, in effect, total pressure curves of uranium-bearing species, since

¹² See ANL-7125, pp. 121-122 for previous report.

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FIG. III-4. Total Pressure of Uranium-Bearing Species as a Function of Urania Composition. (X, O—this work; Δ—calculated, from Eq. 1, this report, and from Eq. 1, ANL-7125, p. 119.)

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FIG. III-5. Partial Pressure of Monatomic Oxygen as a Function of Urania Composition. (Open symbols—this work; filled symbols—calculated, from Eq. 12, this report, and from Eq. 1, ANL-7125, p. 119.)

the contributions from the species $O(g)$ and $O_2(g)$ are negligible. The triangular end-points represent the total pressures of uranium-bearing species at the hypostoichiometric urania phase boundary,¹³ as calculated by means of Eq. 1. As a result of the current investigation, some of the isotherms have been extended into the hyperstoichiometric urania region. It is of interest to note that minima in the total pressures occur in the vicinity of stoichiometric urania. It will be recalled from earlier discussions¹⁴ that UO is the predominant gaseous species in the far hypostoichiometric region, and that its partial pressure decreases rapidly as the oxygen content of the solid increases. Conversely, UO_3 increases in partial pressure as the oxygen content of the solid increases; UO_3 becomes the predominant gaseous species in the far hyperstoichiometric region. The minima in the total pressure curves are, of course, to be associated with compositions corresponding to equilibrium congruent vaporization. However, the data are not accurate enough to determine these compositions as precisely as can be done by the experiments described above in Part 2c.

The partial pressures of oxygen shown in Figure III-5 (open points and crosses) were computed¹² from the moisture content of the exit carrier gas streams.¹⁵ The filled points give the oxygen partial pressures at the hypostoichiometric urania phase boundary. The latter pressures were calculated by the equation

$$\log P_{O_2} \text{ (atm)} = 7.59 - 40,980/T, \quad (12)$$

obtained in the mass-spectrometric effusion study of the uranium-uranium two-phase system.⁷

Of considerable interest in these results is the fact that the isotherms rise less and less steeply at the stoichiometric composition as the temperature increases. This behavior has important consequences for defect models¹⁶ and implies that stoichiometric urania is intrinsically disordered with equal numbers of vacancies and interstitials.

One may use the data of Figure III-5 to obtain a preliminary value of ~ -58 eu for the relative partial molar entropy of solution of diatomic oxygen in

stoichiometric urania in the experimental temperature range. Various values obtained by other workers for hypostoichiometric urania in the range 900 to 1400°C have been summarized by Hagemark;¹⁷ they seem to extrapolate to the range -7 to 20 eu for stoichiometric urania. The contrast between these results requires further theoretical examination.

It should be noted that some of the data points, designated by crosses in Figures III-4 and III-5, were obtained using a modification of our usual transpiration procedure.¹⁸ The modified technique was the following: a 0.5-g charge of urania was placed in a small tungsten crucible ($\sim 1/4$ -in. dia. by $1/2$ in. high) with a perforated bottom through which carrier gas could flow. The crucible was press-fitted into a vapor-deposited-tungsten condenser tube. The condenser tube was then lowered into the transpiration apparatus and a run was conducted in the usual manner. Upon completion of a run, the condenser tube and crucible were removed as a unit from the apparatus and then separated from each other. The O/U ratio of the urania residue in the crucible and the total pressure of uranium-bearing species (from the deposit in the condenser tube) were then determined in the usual manner. It is apparent from Figures III-4 and III-5 that the results obtained by this modified technique are in reasonable agreement with those obtained by our usual procedure. The modified technique should prove generally useful in transpiration and may be particularly useful with plutonium compounds because (1) a relatively small charge is required, thereby hastening the attainment of equilibrium, and (2) the residual solid and the condenser can be simultaneously removed from the furnace for analysis upon completion of an experiment.

After a few more measurements the transpiration study will be written up for journal publication. It is believed that the currently available data can be fitted by an improved model in terms of vacancies, interstitials, and their energies of formation and interaction.

3. Fuel Materials for Fast Breeder Reactors (P. E. BLACKBURN, S. F. BANASZEK)

A review and an evaluation of the literature on the plutonium-uranium-oxygen and the plutonium-ura-

nium-carbon systems are being carried out. The objective is to delineate for these systems questionable or unknown areas of high-temperature thermodynamic study which remain to be investigated. The review of

¹³ Compositions were based on Eq. 1 of ANL-7125, p. 119.

¹⁴ ANL-6925, pp. 166-167.

¹⁵ T. L. Markin, at Harwell, England, using the H_2 - H_2O equilibration technique, has obtained results in good agreement with those shown in Figure III-5 (private communication).

¹⁶ J. S. Anderson, "Nonstoichiometric Compounds," Ad-

vances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, Ch. 1, p. 6.

¹⁷ K. Hagemark, KR-67, Institutt for Atomenergi, Kjeller Research Establishment, Kjeller, Norway, February 1964.

¹⁸ ANL-6900, p. 214; ANL-6925, p. 171.

the oxide system is essentially completed and that for the carbide system is under way.

The review thus far indicates that measurements of the activities of the anionic components in these

ternary systems would be very desirable. Accordingly, a gas-solid equilibration apparatus (similar to the transpiration apparatus discussed in Part 2d) is being constructed for such measurements.

B. PREPARATION OF REACTOR MATERIALS—CERAMIC FUELS

(P. A. NELSON, A. D. TEVEBAUGH, J. D. BINGLE)

The motivations for our study of the preparation of ceramic fuels are to develop preparation procedures which economically fit into appropriate fuel cycles, and to make well-defined fuels for further experimental studies, particularly irradiation studies. Both objectives may be served by a single research program. At the present time, efforts are being directed toward procedures for preparing carbide fuels.

The fluidized-bed technique appears to be especially attractive for preparation of carbide fuels; it affords efficient gas-solids contacting and the product is a

powder which can be directly fabricated into pellets. Two fluidized-bed processes are being developed for preparing carbides: (1) carburization of hydrided uranium or uranium-plutonium alloy with hydrocarbon-hydrogen gas mixtures to form UC or (U,Pu)C, and (2) conversion of (U,Pu)O₂ to (U,Pu)C by reaction with carbon or methane. The former problem is currently requiring the larger effort, whereas the latter is a small effort aimed at developing methods of closing the carbide fuel cycle.

1. Preparation of Carbides by Metal-Hydrocarbon Reaction

a. THERMOBALANCE STUDIES (S. VOGLER, P. KRAUSE)

Knowledge of the reaction thermodynamics for the formation of UC and (U,Pu)C by reaction of the metal or alloy with hydrocarbon gases is important to the rational development of processes employing these reactions. A detailed discussion of the reaction thermodynamics involved was presented in the preceding summary report, ANL-7125, pp. 124-125. It was indicated that excessive carburization of (U,Pu)C by the reaction

can be prevented by maintaining the CH₄ concentration at less than the equilibrium value for this reaction. Thermobalance experiments are being conducted in order to determine a more precise value of the equilibrium CH₄ concentration than can be obtained by calculations based on currently available free energy data.

A description of the thermobalance equipment and procedure was reported previously (see ANL-7055, p. 90). Briefly, the procedure consists of reacting about 3 g of uranium-plutonium alloy with hydrogen in the thermobalance to yield finely divided hydride, and then reacting the hydride with a hydrogen-hydrocar-

bon mixture. The carburizing gas flow is started as soon as hydriding is complete to prevent sintering as the temperature is raised. The change in weight is recorded as a function of time. A gain in weight of the sample beyond that calculated for the monocarbide is indicative of the formation of the sesquicarbide. Formation of significant amounts of sesquicarbide (>5 w/o) can be confirmed by X-ray diffraction analysis.

It was previously reported (ANL-7125, pp. 125-127) that at 750°C, the use of a 1 v/o methane-hydrogen gas mixture at a total pressure of 1 atm resulted in the formation of the sesquicarbide. This result indicates that for the reaction

ΔG is at least -4 kcal/mole of (U,Pu)₂C₃.

In a recent experiment carried out at 770°C, carburizing was initiated with a hydrogen-0.9 v/o methane gas mixture at a total pressure of 1 atm. The reaction proceeded to the stoichiometric weight gain and beyond, indicating that at these conditions (U,Pu)₂C₃ was the equilibrium phase. However, when the methane concentration was lowered to 0.75 v/o, the weight became constant. This result indicated that (U,Pu)₂C and (U,Pu)C were in equilibrium at approximately 0.75 v/o methane, and on the basis of this value the free energy change for the reaction

was calculated to be -4.4 kcal/mole of $(\text{U}, 20 \text{ w/o Pu})_2\text{C}_3$ at 770°C . In another experiment at 810°C , the equilibrium methane concentration in hydrogen was determined to be 0.6 v/o. From this value, ΔG is calculated to be -4.2 kcal/mole of sesquicarbide at 810°C . Further experiments of this type are planned in order to determine the equilibrium gas phase composition at various temperatures and plutonium concentrations. Modifications in the thermobalance reaction vessel have been made to permit reaction and handling of the product in an inert atmosphere. This should minimize the concentrations of impurities in the product and should permit better interpretation of data.

B. PREPARATION OF UC IN A FLUIDIZED-BED REACTOR (P. NELSON, J. GRAAE,¹⁹ C. LEHMANN, K. WILLIAMS²⁰)

The experimental program for the preparation of UC and $(\text{U,Pu})\text{C}$ by the fluidized-bed technique is directed toward exploring the operating conditions which appear most likely to yield stoichiometric monocarbide at high production rates. These conditions, which were discussed in the preceding summary report (ANL-7125, pp. 127–128), are: temperature, 700 to 900°C ; pressure, 5 to 10 atm; and fluidizing gas, 2 to 10 v/o methane in hydrogen. Because of the complications in operating experimental equipment with plutonium, equipment design and operational concepts are being tested in preparations of uranium monocarbide. The UC experiments are being carried out in a closed reactor system mounted in an open hood, whereas the $(\text{U,Pu})\text{C}$ experiments (described below) are being conducted in a glovebox.

A semiworks-scale fluidized-bed reactor (see Figure III-6) with an internal diameter of $2\frac{1}{2}$ in. was installed and is now being used for the preparation of UC on a 2 -kg scale. (Previously, UC was prepared on a 200 -g scale in a $1\frac{5}{8}$ -in. dia. reactor.) The new reactor, which is capable of operation at pressures up to 10 atm and temperatures up to 900°C , is constructed of type 304 stainless steel. It has a jacketed heating section which is pressurized with argon to balance the internal pressure and thus minimize the stress on the heated wall. The reactor was designed to be operated in an air environment and to discharge the product by pneumatically conveying it through a discharge tube to a product receiver that can be removed and opened in a helium atmosphere glovebox.

Run conditions and results of the shakedown runs

with the $2\frac{1}{2}$ -in. dia. reactor are given in Table III-3. Uranium rods, $\frac{3}{8}$ in. in dia. by 1 in. long, were charged to the reactor through a charging lock. After hydriding the uranium to completion, as indicated by unchanging hydrogen pressure, the powdered UH_3 was carbided at 15 psig. (This modest pressure was used to conserve hydrogen, since equipment for recirculation of the off-gas had not yet been installed.) The methane concentration was such that UC was the equilibrium solid phase and the higher carbides would be expected to be unstable. The methane concentrations in the inlet and outlet streams were determined by infrared analyses.

The mean particle size obtained in these runs was usually about 15 to 20μ . In the case of run UC-9S, however, the uranium was hydrided and dehydrided three times by cycling the temperature, with the result that 97 w/o of the product was finer than 20μ . Methane utilization was usually about 50% near the beginning of a run and tapered off to 10 to 20% after 2 or 3 hr. The fine particle size in run UC-9S, however, resulted in a methane utilization of nearly 100% for the first $1\frac{1}{2}$ hr of carburization; that is, the methane concentration of the off-gas stream was zero, within the accuracy of the infrared analyzer.

In general, the operation of the reactor was satisfactory. However, some difficulty was encountered in fluidization and in the pneumatic discharge of the product. Incomplete fluidization was often evidenced by a low pressure drop across the bed and erratic methane utilization. This condition was temporarily relieved by applying a mechanical shock to the reactor. The use of pulsed fluidizing gas flow was also beneficial, although it did not entirely alleviate the problem of incomplete fluidization. Repeated attempts were required to discharge the product from the reactor; occasionally, a hydriding cycle was also required to react uranium metal that presumably had sintered because of partial immobility of the fluidized bed during carbiding. These difficulties are attributed to the fineness of the powder resulting from the hydriding of uranium alone. Since hydriding uranium-plutonium alloy results in larger particles, it is believed that these difficulties may not be encountered when reactors similar to the semiworks reactor are used for the preparation of $(\text{U,Pu})\text{C}$. This belief is supported by observations made during the preparation of $(\text{U,Pu})\text{C}$ in the small-scale, $1\frac{5}{8}$ -in. dia. reactor (see below).

Since the primary purpose of these initial runs in the $2\frac{1}{2}$ -in. dia. reactor was to test the equipment, no special efforts were made to insure products of high purity. (In previous work, described in ANL-7125, pp. 127–128, stoichiometric UC with an oxygen content

¹⁹ Design Group, Chemical Engineering Division.

²⁰ Co-op student, Purdue University.

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FIG. III-6. Semiworks Fluidized-Bed Reactor for Carbide Synthesis. (Carbiding conditions: up to 900°C, 10 atm.)

as low as 0.08 w/o was prepared.) The main sources of impurities in the recent runs were (1) the reagent gases and (2) the glovebox atmosphere (<5 ppm each of water and oxygen) to which the products were exposed after removal from the reactor. Work is being initiated to determine the rate of oxidation of these fine UC powders in the helium glovebox atmosphere. Means of protecting the powders by adding a pellet binder that would inhibit oxidation prior to pressing is also being investigated. The binder could possibly be added before the product is removed from the fluidized bed, and thus greatly reduce the oxidation problem.

The reactor system has recently been modified to recirculate the off-gas from the fluidized-bed reactor

and thereby reduce the amount of hydrogen and methane required. This is expected to reduce the impurity level in the gas stream and consequently reduce contamination of the product. After testing of the recirculation system, runs will be initiated at pressures up to 10 atm.

c. PREPARATION OF (U,Pu)C IN A FLUIDIZED-BED REACTOR (E. J. PETKUS, J. O. LUDLOW,¹⁹ C. C. PAYNE)

The present goal for preparation of (U,Pu)C is a high-purity product to demonstrate the feasibility of the fluidized-bed process. A secondary objective of the experiments is to obtain material for irradiation testing.

A helium-atmosphere glovebox system for this work has recently been completed and tested. The two gloveboxes which house the reactor system are shown in Figure III-7. The gloveboxes have a total volume of about 250 cu ft and are equipped with 52 gloveports. Other features include an interconnecting transfer lock, a vacuum lock containing a plutonium bagout mechanism, and several other mechanisms for ingress and egress of materials. Purification of the atmospheres of the gloveboxes is accomplished by sorption of impurities by activated charcoal at liquid nitrogen temperatures. The activated charcoal trap is preceded by a Molecular Sieve dryer which prevents excessive ice formation in the charcoal trap. This method of purification, which requires the use of helium rather than argon to avoid liquification of the inert gas in the cold trap, was chosen because it is capable of maintaining an inert gas at very high purity, and is safe for operation at the negative pressures that are required for plutonium gloveboxes. (In argon purification systems,

TABLE III-3. URANIUM CARBIDE SYNTHESIS IN SEMIWORKS REACTOR

	UC-6S	UC-7S	UC-8S	UC-9S
Charge (g)	1000	1700	2000	2000
Hydriding cycles	1	1	1	3
Inlet methane conc. (v/o)	5.0	6.2	5.0	5.0
Carbiding time (min)	340	565	511	460
Carbiding temperature (°C)	750	750	800	800
Carbiding pressure (psig)	15	15	15	15
Total product transferred (g)	1035	1804	1922	1700
<i>Product analysis (w/o)</i>				
Carbon ^a	4.0	4.8	4.2	4.6
Oxygen ^b	0.40	0.48	0.50	0.50

^a Stoichiometric UC contains 4.8 w/o carbon.

^b The high oxygen contents, which are not typical for this process, are due to impurities in the gas and, probably, to reaction with the glovebox atmosphere subsequent to product removal from the reactor.

FIG. III-7. Glovebox Facility for (U,Pu)C Preparation.

gettering materials such as uranium, calcium, or titanium react violently with high concentrations of air which may be inadvertently admitted in a negative pressure system.) Another advantage of the use of charcoal rather than a chemical gettering material is that charcoal can be regenerated repeatedly by simply heating to modest temperatures and evacuating the vessel. This is especially important in applications involving plutonium or other toxic substances, wherein waste handling and disposal are expensive and hazardous. The purification system, which is operated at a recirculation rate of about 10 cfm and a pressure of -0.6 in. of water relative to the exterior pressure, is capable of maintaining the helium atmosphere at a level of purity of ~6 to 7 ppm oxygen and 1 to 2 ppm water.

The larger of the two gloveboxes in Figure III-7 houses the fluidized-bed reactor in which (U,Pu)C powder is prepared. The smaller box will be used for testing the sinterability of the carbides produced in the fluidized-bed reactors and for preparing carbide pellets for irradiation studies.

Initially, UC and (U,Pu)C are being produced on a scale of 300 to 500 g in a 1½-in. ID fluidized-bed reactor by first hydriding uranium metal or uranium-plutonium alloy and then carburizing with methane-hydrogen fluidizing gas. The design of the reactor is similar to that of the semiworks reactor (Figure III-6) in that the fluidizing gas is introduced through a tube at the top of the reactor, and is discharged in a conical section at the bottom of the reactor. (This configuration is discussed in greater detail in the following subsection.) This reactor differs from the semiworks reactor, however, in that it does not have a jacket and is limited to an operating pressure of 5 atm at 800°C. As a consequence of not having a jacket, the reactor is light enough to be manipulated in the glovebox. In these small-scale preparations, the capability of thoroughly cleaning the reactor between runs is important in order to prevent contamination from residual car-

bide that is inadvertently oxidized. While the reactor is open for removal of the product, the fine carbide powder can react with low concentrations of water and oxygen in the glovebox atmosphere. To remove powder residues left on the walls of the reactor, a motorized wire brush is used.

Three runs were completed on preparation of UC in the 1½-in. dia. reactor to test the equipment. The results of these runs are shown in Table III-4. Approximately 6 to 8 hr was required to reach the stoichiometric equivalent carbon content of 4.80 w/o. The oxygen concentrations, although in an acceptable range for powders to be used for producing pellets, were not as low as those obtained previously in fluidized-bed experiments (ANL-7125, pp. 127-128); this may have been due to uptake of oxygen during the unloading and sampling of the UC product, despite the fact that the glovebox atmosphere was very pure, as noted above. The addition of a combination binder and oxidation inhibitor to the UC powder prior to exposure to the glovebox atmosphere may alleviate this problem.

Three preparations of (U, 15 w/o Pu)C on a 300-g scale have also been completed in this reactor. The following carbiding conditions were employed: gas concentration, 10 v/o CH₄-90 v/o H₂; total pressure, 4 atm; bed temperature, 750°C. The rate of reaction for the formation of the (U,Pu)C was determined continuously by monitoring the methane concentration of the incoming and outgoing fluidizing gas streams with an infrared analyzer. The extent of reaction during an experiment was obtained by integrating the rate of reaction over the time interval of interest.

Under the conditions used, about 10 to 12 hr was required to produce stoichiometric monocarbide (4.80 w/o carbon). After an initial reaction period of ~6 hr, the rate of reaction became relatively low at a carbon content of about 4.1 w/o. An additional hydriding of the residual U-15 w/o Pu alloy and cooling to room temperature was used to increase the reaction rate.

TABLE III-4. UC PREPARATION IN (U,Pu)C EQUIPMENT

Gas composition: 5 v/o CH₄-95 v/o H₂
 Temperature: 750°C
 Pressure: 4 atm

Run No.	C/U Ratio ^a	Run Time (hr)	Fluidizing Gas Velocity (ft/sec)	Product Analyses			
				Total C (w/o)	Oxygen (w/o)	Nitrogen (w/o)	Equivalent C ^b (w/o)
UCF-59	11.1	8	0.50	4.70	0.18	0.067	4.90
UCF-61	6.4	6	0.40	4.55	0.29	0.007	4.78
UCF-60	4.2	3	0.50	4.08	0.30	0.048	4.34

^a Atom ratio of carbon in total fluidizing gas to uranium in charge.

^b Oxygen and nitrogen are soluble in UC and replace carbon in the lattice; equivalent C = w/o C + (12/16) w/o O + (12/14) w/o N; stoichiometric UC contains 4.80 w/o carbon.

The additional hydriding was carried out in all runs except the first one.

The product from the first run, which was terminated after 6 hr, was hypostoichiometric in carbon content, whereas the other two products were close to the stoichiometric composition. The carbon contents of the products of the three runs were 4.11 w/o, 4.96 w/o, and 4.89 w/o, respectively. The oxygen impurity levels were very low for these runs, averaging about 500 ppm or 0.05 w/o. One sample of the product from the second run contained only 160 ppm oxygen. It is now believed that, in general, the carbide produced by this process has a low oxygen content (<500 ppm) when it is removed from the reactor, but that significant amounts of oxygen may be introduced during unloading and sampling of the product for analysis. Particle-size determinations of the products of these (U,Pu)C preparations indicated a volume-mean size of 65 to 75 μ , about four or five times the size of UC prepared by this method (see ANL-7055, p. 89). Thus, lower rates of oxidation of (U,Pu)C than of UC would be expected in the glovebox atmosphere.

The effect of temperature on the reaction rate was explored in one of the three runs. The rate was significantly lower at carbiding temperatures of 550 to 650°C than it was at 750°C. This is in agreement with previous findings (ANL-7055, p. 90).

Additional data on the above experiments on preparation of (U,Pu)C as well as data on experiments that are currently under way will be reported in the next progress report. Particular attention will be given in future runs to reducing the time required for carbiding.

d. FLUIDIZATION TESTS (E. J. PETKUS, J. E. PECK)

The fluidized-bed reactors currently being used in this program are of a different design than those in general use. Introduction of the fluidizing gases into the bed is usually accomplished by means of a porous metal plate, a metal plate with drilled holes, or a gas entry tube at the bottom of a cone; in these systems the gases are preheated by an auxiliary heater adjacent to the fluidized-bed reactor. The current design employs a tube running down through the center of the fluidized-bed reactor to introduce the gases and disperse them in a bottom conical section. This design eliminates pockets and small holes where finely divided powder could collect; it alleviates problems of differential thermal expansion.

In the present process, since the centers of the particles are metallic, the particles must be kept in a vigorously fluidized state during carbiding to prevent sticking or sintering of the particles into a nonfluidiz-

able mass. Previous work in a 1-in. dia. fluidized-bed reactor used for UC synthesis showed that sintering occurred when fluidization was not sufficiently vigorous. This sintering appeared to be caused by insufficient fluidizing gas velocity which resulted in pockets of immobile particles. To define the problems associated with the new reactor design, a simulated reactor column made of clear plastic and having about the same dimensions and physical arrangement as the semiworks reactor was built and tested.

Since the tests were to be carried out in an air environment, the UC particles were carefully oxidized to produce a UO_2 coating on the surface prior to the tests. This minimized the pyrophoricity in air while maintaining the same average particle size ($\sim 15 \mu$). Incipient fluidization of the particles in the plastic column did not occur until a superficial velocity of 0.20 ft/sec was reached. (This agreed with data obtained in early UC preparation runs at 600 and 700°C, in which occasional sintering of uranium metal particles occurred at a superficial velocity of 0.25 ft/sec.) A superficial helium gas velocity of 0.50 ft/sec provided good fluidization of the particles; there was vigorous bumping of the bed and good vertical movement of the individual particles along the wall. No pockets of immobile particles were observed when the fluidizing gas tube was lowered to within $\frac{1}{8}$ in. of the bottom of the cone. When the fluidizing tube was raised more than $\frac{1}{8}$ in. above the bottom of the cone, a layer of immobile particles began to collect on the bottom of the cone. The presence of the fluidizing gas tube and the product draw-off tube did not appear to be detrimental to the fluidization characteristics of the bed; there did not appear to be any channeling of gas around these tubes.

It is important to be able to remove all of the product after each fluidized-bed preparation in order to prevent cross contamination of individual UC products. To test the efficiency of product removal, a vacuum of about 12 in. Hg was applied to the draw-off tube of the plastic column while maintaining the fluidizing gas velocity at ~ 0.50 ft/sec. If the draw-off tube was within $\frac{1}{4}$ in. of the bottom of the cone, all of the material was removed from the bed.

These tests at room temperature showed the soundness of the basic design of the reactors used for carbide synthesis. The entire contents of the reactors can be kept in a vigorously fluidized state to prevent sintering. There should be no channeling around the inserted tubes to hinder fluidization and gas utilization. Finally, automatic and complete removal of the finely divided carbide products from the reactor appears to be feasible.

2. PREPARATION OF CARBIDES BY CONVERSION OF OXIDES

(P. NELSON, J. GRAAE¹⁹)

The fluidized-bed process to convert $(U,Pu)O_2$ to $(U,Pu)C$ is in the planning and design stage. One source of $(U,Pu)O_2$ for this process would be the UF_6 - PuF_6 product of the fluoride volatility fuel reprocessing cycle that is being studied by other groups in this Division. The $(U,Pu)O_2$, on the basis of experimental data for UO_2 , is expected to have a high bulk density. It is contemplated that carbon will be blended with the oxide during conversion of UF_6 - PuF_6 to $(U,Pu)O_2$, after which the $(U,Pu)O_2$ -carbon mixture will be converted in a high-temperature (1500 to 1700°C) fluidized bed to the monocarbide. At this

point, excess carbon, if present, should be removable by a fluidizing gas of hydrogen at $\sim 1000^\circ C$. An alternative approach would be to react a methane-hydrogen gas mixture with $(U,Pu)O_2$ particles in a fluidized bed at high temperatures and pressures. It is believed that formation of carbides, rather than carbon coating of the oxide particles, can be attained by proper selection of the process variables. Either of these oxide conversion processes may be capable of producing dense spherical particles which would be suitable for the vibratory compaction method of fuel densification.

C. CALORIMETRY (W. N. HUBBARD, H. M. FEDER, M. ADER)

For many substances of interest in high-temperature chemistry and nuclear technology, thermodynamic data are lacking or they lack acceptable accuracy. To fill in the significant gaps in our knowledge, the present research program in calorimetry was undertaken.

The determination of standard enthalpies of formation, ΔH_f° , of substances is an essential foundation for further thermodynamic studies. When applicable some of these enthalpies have been determined by oxygen bomb calorimetry, a technique which has been developed to a high degree of precision and accuracy. Many of the materials of interest are difficult to burn in oxygen, however, and can not be studied by this method. For these difficult cases the techniques of the bomb calorimetric method have been successfully modified so that fluorine may be used as an oxidant with similar precision and accuracy. A further outgrowth of the achievement of performing precision bomb calorimetry with fluorine has been the development of techniques for using other reactive gases, such as PF_3 and NF_3 , and for fluorine flow calorimetry.

The accumulation of enthalpy-of-formation data for elemental fluorides is both a necessary preliminary to the general use of fluorine reaction calorimetry and a valuable program on its own merit. To date, enthalpy-of-formation values have been determined for 25 elemental fluorides. The enthalpies of formation of the following substances have also been determined by

fluorine bomb calorimetry: boron nitride, quartz and vitreous silica, α - and β -silicon carbide, and the diborides of zirconium, hafnium, niobium, and tantalum. An extensive program of determining enthalpies of formation of uranium compounds is under way; a similar program for plutonium compounds has been started.

As in the previous report (ANL-7125), tables of calorimetric data are not presented here. Instead, derived data will be presented or, where appropriate, the abstract of the manuscript describing the research will be quoted. Occasionally, when an enthalpy-of-formation value is published in its complete form in a journal article, it will be slightly different from the value given in this report owing to minor refinements in calculation. Therefore, before the data are put to exacting use, the journal article should be checked. Detailed data may be obtained by request to the investigators.

To determine thermodynamic properties at high temperatures, one combines values of enthalpies of formation at $25^\circ C$ with values of the enthalpy increments to the higher temperatures. A drop calorimeter for making enthalpy increment measurements to $1500^\circ C$ has been assembled and tested with measurements on a standard sample of synthetic sapphire. It is now being used for measurements on a series of uranium compounds. A calorimeter for measuring enthalpy increments to $2500^\circ C$ has also been designed and is being constructed.

1. The Standard Enthalpies of Formation of Crystalline and Amorphous Boric Oxides (G. K. JOHNSON)

The considerations which led to the determination of the enthalpy of formation of boric oxide, B_2O_3 , by fluorine bomb calorimetry were outlined previously.²¹ The experimental portion of this work is essentially complete.

Crystalline B_2O_3 was grown from seed in a melt resulting from the partial dehydration of high-purity boric acid. The product was pulverized, dehydrated, and stored in a helium-atmosphere glovebox (H_2O , ~ 0.1 ppm). Amorphous B_2O_3 was prepared in the glovebox by melting a portion of the crystalline B_2O_3 and pulverizing the quenched melt. X-ray powder diffraction

crease in weight of the nickel crucible (NiF_2 formation) were determined after each combustion. The gaseous combustion products were examined by mass spectrometry, gas chromatography, and infrared spectrometry to determine if any boron oxyfluorides had been produced. No evidence for combustion products other than BF_3 and O_2 was found.

Values of -3455.6 ± 1.9 and -3505.7 ± 2.1 cal g^{-1} were obtained for the energies of combustion in fluorine of crystalline and amorphous B_2O_3 , respectively. These values include thermal corrections of -1.0 and -2.8 cal g^{-1} , respectively, for the impurities in the specimens.

TABLE III-5. COMPARISON OF CALORIMETRIC DATA FOR BORIC OXIDE

Investigator	Method	$\Delta H_f^\circ_{298}(c)$ (kcal mol ⁻¹)	$\Delta H_f^\circ_{298}(\text{amorph.})$ (kcal mol ⁻¹)	$\Delta H_{tr}^\circ_{298}$ (kcal mol ⁻¹)
Southard ²⁴	Dissolution in H_2O			4.36 ± 0.02
Prosen et al ²⁵	Decomposition of B_2H_6 and dissolution of B_2H_6 in H_2O	-305.34 ± 0.75	-300.98 ± 0.75	^a
Good and Mansson ²⁶	Combustion of B in O_2 and dissolution of product in $HF(aq)$	-304.10 ± 0.40	-299.74 ± 0.40	^a
Fasolino ²⁷	Dissolution in H_2O^b	-303.63 ± 0.42	-299.30 ± 0.43	4.33 ± 0.06
This work	Combustion in F_2	-303.02 ± 0.49	-299.52 ± 0.51	3.50 ± 0.33

^a Southard's value was assumed.

^b This is not a completely independent determination. Fasolino accepted Good's value for $\Delta H_f^\circ(H_3BO_3, c)$ and redetermined the heats of solution of $H_3BO_3(c)$, $B_2O_3(c)$, and $B_2O_3(\text{amorph.})$.

analyses confirmed that one preparation was crystalline (hexagonal) and the other amorphous; microscopic examination indicated the former to be at least 99.9% crystalline. The results of chemical and spectrographic analyses for impurity content follow (in ppm): crystalline B_2O_3 -C (38), H (170), Fe (300), Si (50), Mg (5); amorphous B_2O_3 -C (107), H (270), Fe (200), Si (50), Mg (5).

The fluorine combustions were carried out in a two-chambered reaction vessel²² after it was found that crystalline B_2O_3 prefluorinates to a nonreproducible extent. A mixture of sulfur and powdered boron was used as an ignition aid. The sample and ignitor were contained in a small crucible (spun from 10-mil nickel foil) which was suspended in the middle of the bomb from a nickel ring. This arrangement helped to achieve nearly complete combustion because the limited thermal contact between the crucible and bomb caused the sample to burn hotter. The amount of boric oxide residue and the in-

These energies of combustion and the enthalpy of formation of BF_3 ²³ (-271.65 ± 0.22 kcal mol⁻¹), were used to calculate $\Delta H_f^\circ_{298,15}(B_2O_3, c) = -303.02 \pm 0.49$ kcal mol⁻¹ and $\Delta H_f^\circ_{298,15}(B_2O_3, \text{amorph.}) = -299.52 \pm 0.51$ kcal mol⁻¹.

In Table III-5, the results of this investigation are compared with results²⁴⁻²⁷ obtained by solution calorimetry. Our value for $\Delta H_f^\circ(B_2O_3, \text{amorph.})$ compares favorably with that obtained from the combined data of Good and Mansson²⁶ and Fasolino.²⁷ However, our values for $\Delta H_f^\circ(B_2O_3, c)$ and the enthalpy of transition, ΔH_{tr}° , do not agree with the other results. In an attempt to resolve these discrepancies, Fasolino (National Research Corporation) is currently making solution calorimetric measurements on specimens of crystalline and amorphous B_2O_3 that we have prepared.

²³ G. K. Johnson, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.* **70**, 1 (1966).

²⁴ J. C. Southard, *J. Am. Chem. Soc.* **63**, 3147 (1941).

²⁵ E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, *J. Res. Natl. Bur. Std.* **62**, 43 (1959).

²⁶ W. D. Good and M. Mansson, *J. Phys. Chem.* **70**, 97 (1966).

²⁷ L. G. Fasolino, *J. Chem. Eng. Data* **10**, 373 (1965).

²¹ ANL-7125, p. 133.

²² R. L. Nuttall, S. S. Wise, and W. N. Hubbard, *Rev. Sci. Instr.* **32**, 1402 (1961).

2. The Standard Enthalpy of Formation of Tungsten Hexafluoride

(P. A. G. O'HARE)

Bomb calorimetric combustions of high-purity tungsten sheet (0.005 in. thick) in fluorine were performed by the same method²⁸ used for the combustion of molyb-

108-9610

FIG. III-8. Sample Arrangement for Combustions of Tungsten in Fluorine. A—nickel support rod; B—tungsten wire sling; C—tungsten sample; D—tungsten ignition wire; E—insulated electrode.

denum in fluorine. (Trial experiments in a glass bomb²⁹ had shown that the combustion was vigorous and lasted

²⁸ J. L. Settle, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.* **65**, 1337 (1961).

²⁹ R. L. Nuttall, M. A. Frisch, and W. N. Hubbard, *Rev. Sci. Instr.* **31**, 461 (1960).

for about 1 min.) Figure III-8 is a sketch of the sample arrangement. The initial fluorine pressure in the bomb was 115 psia. Combustion was initiated by passing an electrical current through the tungsten ignition wire. In general, about 99.5 % of the sample was consumed; only small beads of unreacted tungsten (approximately 3 mg) remained. The gaseous reaction product, after removal of excess fluorine, was identified by infrared analysis³⁰ as tungsten hexafluoride.

Eight acceptable calorimetric experiments were performed from which an average value, $-2233.1 \text{ cal g}^{-1}$, was calculated for the energy of combustion of the sample in fluorine. The standard deviation of the mean was 1.2 cal g^{-1} . A thermochemical correction of $1.2 \pm 0.2 \text{ cal g}^{-1}$ for trace impurities in the sample was made. Thus, the standard energy of combustion of tungsten in fluorine, according to Eq. 1, is $-2231.9 \pm 1.2 \text{ cal g}^{-1}$.

This energy of combustion was used to derive $\Delta H_f^\circ_{298}(\text{WF}_6, \text{g}) = -411.5 \pm 0.4 \text{ kcal mol}^{-1}$. The uncertainty is an uncertainty interval³¹ equal to *twice* the combined standard deviations arising from all known sources.

The enthalpies of vaporization of $\text{WF}_6(\ell)$ and fusion of $\text{WF}_6(\text{c})$ are 6.2 and 0.5 kcal mol^{-1} , respectively.³² These values in conjunction with our value for $\Delta H_f^\circ(\text{WF}_6, \text{g})$ give $\Delta H_f^\circ(\text{WF}_6, \ell) = -417.7 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{WF}_6, \text{c}) = -418.2 \pm 0.6 \text{ kcal mol}^{-1}$. Myers and Brady³³ measured the enthalpy of solution of $\text{WF}_6(\text{g})$ in aqueous NaOH, and derived a value of $-416 \pm 4 \text{ kcal mol}^{-1}$ for $\Delta H_{f298}^\circ(\text{WF}_6, \text{g})$. JANAF³⁴ revised this value to $-421 \pm 4 \text{ kcal mol}^{-1}$, but both values are in disagreement with the present measurements. This discrepancy, of unknown origin, parallels that observed²⁸ previously for MoF_6 . The determination reported in this paper is based on *direct* combination of the elements in a well-defined reaction, and is thus regarded as being more reliable.

A note based on this work has been published in *J. Phys. Chem.* **70**, 3353 (1966).

³⁰ T. G. Burke, D. F. Smith, and H. A. Nielsen, *J. Chem. Phys.* **20**, 447 (1956).

³¹ F. D. Rossini, *Chem. Rev.* **18**, 233 (1936).

³² E. J. Barber and G. H. Cady, *J. Phys. Chem.* **60**, 505 (1956).

³³ O. E. Myers and A. P. Brady, *J. Phys. Chem.* **64**, 591 (1960).

³⁴ "JANAF Thermochemical Tables," The Dow Chemical Company, Midland, Michigan, 1963.

3. The Standard Enthalpy of Formation of Phosphorus Pentafluoride

(P. A. G. O'HARE)

A paper bearing the following title has been submitted for publication:³⁵ "Fluorine Bomb Calorimetry. Part 18. The Standard Enthalpy of Formation of Phosphorus Pentafluoride and the Enthalpies of Transition Between Various Forms of Phosphorus. Thermodynamic Functions of Phosphorus Pentafluoride Between 0 and 1500°K." The abstract is as follows:

"The energies of combustion in fluorine of α -white phosphorus and three modifications of red phosphorus—amorphous I, crystalline IV, and crystalline V—were measured. With the adoption of α -white

phosphorus as standard state, the standard enthalpy of formation of $\text{PF}_5(\text{g})$ at 25° was calculated to be $-380.8 \pm 0.3 \text{ kcal mole}^{-1}$. The enthalpies of transition at 25° for the following processes are reported: $\text{P}(\alpha\text{-white}) \rightarrow \text{P}(\text{amorphous red I})$, $\Delta H_t = -3.9 \pm 0.4 \text{ kcal g-atom}^{-1}$; $\text{P}(\alpha\text{-white}) \rightarrow \text{P}(\text{red V})$, $\Delta H_t = -3.9 \pm 2.0 \text{ kcal g-atom}^{-1}$; $\text{P}(\text{red IV}) \rightarrow \text{P}(\text{red V})$, $\Delta H_t = -1.2 \pm 1.0 \text{ kcal g-atom}^{-1}$. High-temperature thermodynamic functions for $\text{PF}_5(\text{g})$ are also reported."

4. The Enthalpy of Formation of Carbon Tetrafluoride (Tetrafluoromethane)

(E. GREENBERG)

108-9171

FIG. III-9. Two-Chambered Combustion Bomb.

The need for determining the enthalpy of formation of CF_4 by direct combustion of carbon in fluorine was discussed previously.³⁶

³⁵ P. A. G. O'Hare and W. N. Hubbard, Fluorine Bomb Calorimetry. Part 18. Standard Enthalpy of Formation of Phosphorus Pentafluoride and Enthalpies of Transition Between Various Forms of Phosphorus. Thermodynamic Functions of Phosphorus Pentafluoride Between 0 and 1500°K, Trans. Faraday Soc., **62**, 2709–2715 (October 1966).

³⁶ ANL-7125, pp. 133–134.

The preparation³⁶ of a sample of natural graphite was completed. Final graphitization and purification of the crude sample were performed by the Union Carbide Corporation. During graphitization, the sample was held at 3000°C for fifteen minutes in a nitrogen atmosphere. Purification was achieved by heating the graphite to a temperature in excess of 2500°C in a chlorine atmosphere, followed by cooling in an atmosphere of nitrogen. The resulting sample has a metallic impurity

content of about 15 ppm, and a total oxygen, hydrogen, and nitrogen content of less than 100 ppm.

A small, nonreproducible amount of spontaneous reaction takes place when graphite is exposed to fluorine. This necessitates the use of a two-chambered combustion bomb which isolates the fluorine from the graphite until the beginning of the calorimetric reaction period. In addition, preliminary experiments had shown that fluorine pressures in excess of 15 atm were required in order to minimize the formation of higher fluorocarbons, such as C_2F_6 and C_3F_8 . A new two-chambered bomb, shown in Figure III-9, was therefore designed and built for use in this and other studies which require high pressures of fluorine. In this design, the fluorine storage chamber is integral with the combustion chamber and has heavy walls throughout. Thus one is able to store fluorine at a pressure such that the final pressure after expansion is >20 atm. (The thin-walled storage cham-

ber of the previous design²² limited this final pressure to <10 atm.) Trials with this bomb indicate that it can be satisfactorily calibrated by the combustion of benzoic acid.

Graphite combustion experiments with the new, high-pressure, two-chambered bomb indicated that the inrush of fluorine from the storage chamber to the combustion chamber caused much of the sample to be blown around. This problem was circumvented by placing the sample in a nickel crucible with vent holes for fluorine circulation, and inserting a restrictive porous plug in the fluorine inlet line. It was also discovered that a soot-like deposit on the bottom of the crucible after combustion was not unburned carbon, but was, in fact, nickel sulfide formed unexpectedly by reaction of the sulfur ignition aid with the crucible. Powdered boron nitride or silicon has been substituted for sulfur with good results. A calorimetric series of graphite combustions is under way.

5. Thermochemistry of Plutonium and Its Compounds (G. K. JOHNSON)

The increasing use of plutonium compounds as nuclear fuels demands that the thermodynamics of these compounds be better understood. The bulk of the present thermodynamic data for plutonium-containing materials is estimated and unreliable; accurate enthalpies of formation are known for only a few plutonium compounds. Our ready access to extensive plutonium facilities and our calorimetric capabilities provide us with the opportunity for obtaining very valuable thermodynamic data for plutonium compounds. The report below briefly discusses plutonium calorimetry with respect to work that has been done, work that is needed, calorimetric techniques, and current plans.

Oxygen bomb calorimetry has been used to determine the enthalpies of formation of PuO_2 ,^{37,38} $PuC_{0.77}$,³⁹ and Pu_2C_3 .³⁹ The value for PuO_2 seems to be well known; however, the values for the carbides are still unreliable owing to uncertainties in sample characterization. The enthalpies of formation of $PuCl_3$,⁴⁰ $PuOCl$,⁴¹ $PuFe_2$,⁴² $PuAl_2$,⁴² $PuAl_3$,⁴² and $PuAl_4$,⁴² have been determined by

³⁷ C. E. Holley, Jr., R. N. R. Mulford, E. J. Huber, Jr., E. L. Head, and C. W. Bjorklund, *Proc. U.N. Inter. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958*, Vol. 6, p. 215.

³⁸ M. M. Popov and M. I. Ivanov, *Sov. J. Atomic Energy* **2**, 439 (1957).

³⁹ E. J. Huber, Jr., Los Alamos Scientific Laboratory, unpublished measurements.

⁴⁰ H. P. Robinson and E. F. Westrum, in "The Transuranium Elements," NNES **14B**, McGraw-Hill Book Co., Inc., New York, 1949, p. 922.

⁴¹ E. F. Westrum and H. P. Robinson, *ibid.*, p. 914.

⁴² V. V. Akachinskii, L. M. Kopytin, M. I. Ivanov, and N. S. Podolskaya, "Thermodynamics of Nuclear Materials," IAEA, Vienna, 1962, p. 309.

calorimetric measurement of appropriate heats of solution in hydrochloric acid. The values are dependent on the enthalpy of reaction^{40, 43} of plutonium metal with hydrochloric acid, a quantity whose uncertainty^{42, 44} has apparently been resolved.⁴⁵ The enthalpy of formation of $PuBr_3$ ⁴⁶ has been determined by a similar method.

The enthalpies of formation of the fluorides, carbides, lower oxides, sulfides, nitrides, hydrides, borides, phosphides, and silicides of plutonium, and of many plutonium alloys are still not known precisely. Thus, any long-range program to obtain enthalpies of formation of plutonium compounds should include these compounds as well as any other compounds and alloys that may be of interest.

The specific calorimetric technique to be used in a given investigation will, of course, depend on the properties of the compound being studied. As a result of our preliminary studies, the three types of calorimetry which seem to be most suitable for plutonium compounds are oxygen bomb calorimetry, halogen bomb calorimetry, and solution calorimetry.

Oxygen bomb calorimetry ought to be applicable to the determination of the enthalpies of formation of the carbides, nitrides, lower oxides, and, possibly, hydrides.

⁴³ V. V. Akachinskii and L. M. Kopytin, *Sov. J. Atomic Energy* **9**, 1051 (1960).

⁴⁴ J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.* **25**, 1423 (1963).

⁴⁵ V. V. Akachinskii, "Thermodynamics," Vol. II, IAEA, Vienna, 1966, p. 561.

⁴⁶ E. F. Westrum in "The Transuranium Elements," NNES **14B**, McGraw-Hill Book Co., Inc., New York, 1949, p. 926.

Fluorine or chlorine bomb calorimetry ought to be applicable to some of the refractory compounds—carbides, nitrides, sulfides, phosphides, silicides, and borides. Present indications are that these plutonium compounds will react with fluorine to give the tetrafluoride and/or the hexafluoride. Even if a single product cannot be obtained, fluorine combustions may still have merit if the ratio of PuF_6 to PuF_4 in the product and the energy of conversion can be determined. A significant advantage of fluorine bomb calorimetry which should not be overlooked is the accumulation of experimental techniques in this laboratory together with many well-established auxiliary enthalpies of formation. This advantage does not exist for chlorine bomb calorimetry. However, as chlorine is reported to give only a single plutonium product, PuCl_3 , it may bring about better characterized reactions. Combustion experiments with both halogens will be tried.

Solution calorimetry may be the most generally applicable of any of the techniques contemplated. Many plutonium alloys can be studied by reaction with hydrochloric or perchloric acid. It is also expected that numerous compounds, e.g., the nitride and sulfide, will react with hot aqueous acids. Of course, the applicability

of these more complex reagents depends on the ability to characterize the valence states of the aqueous plutonium ions.

Although many reactions appear to be suitable for calorimetric measurement, the majority of them have not, as yet, been studied under calorimetric conditions. Two reactions which would be logical starting places for our work are:

These reactions have the special merit that they start with materials that are available in high purity, they are expected to react completely to form well-defined products, and the enthalpies of formation are well known, and thus will serve as a check on our techniques. Furthermore, these reactions serve as necessary adjuncts to the determination of the enthalpies of formation of plutonium compounds by combustion in oxygen or chlorine.

The present plans call for the installation of an existing rotating bomb calorimeter inside an alpha glovebox. With suitable modifications the apparatus is expected to be adaptable to either solution or bomb calorimetry.

6. The Combustion of Thorium in Fluorine (E. VAN DEVENTER, E. RUDZITIS)

Our efforts to obtain a precise value for $\Delta H_f^\circ(\text{ThF}_4)$ have, to date, been unsuccessful. The history of this project is reviewed below.

The physical and chemical properties of thorium and its fluorine combustion product, thorium tetrafluoride, indicated that the technique⁴⁷ developed earlier for combustion of metals which form nonvolatile fluorides might be applied. However, numerous difficulties were immediately encountered. The combustion technique, which involved the use of the fluoride of the metal to be burned, both as a support and as a bomb liner, had been most successful when both the melting point and the density of the metal were lower than that of the metal fluoride. Ideally, the metal, which is liquified by the heat of reaction, burns on top of the fluoride support. This technique has been successfully applied to Cd, Zn, Mg, Al, Y, Gd, Ho, and Ni even though conditions were not always ideal. Thorium, however, has a density (11.7 g cm⁻³) which is almost twice that of its fluoride (6.1 g cm⁻³) and a melting point (1750°C) which is appreciably higher than the melting point of ThF_4 (1100°C). As a result, thorium, on melting, has a strong tendency to coalesce into spheres (due to surface tension) and submerge into the molten ThF_4 . This, in turn, required

that the ThF_4 liners and supports had to be mechanically disintegrated after each combustion and assayed for their content of unburned metal by the hydrogen evolution method. But thorium does not liberate hydrogen stoichiometrically when treated with aqueous $\text{HCl-H}_2\text{SiF}_6$ (yields are 90 to 95 %), and consequently, combustions had to be very nearly complete so that the uncertainties associated with the hydrogen evolution method would be small. Finally, sintered or solidified ThF_4 is an extremely hard material which was readily contaminated by metal particles resulting from the abrasion of bomb walls, dies, tools, etc.

In spite of the difficulties encountered, the developmental work was sufficiently successful to warrant proceeding with calorimetric combustions. In the most recent series, the combustion yield in four out of six combustions exceeded 98 %; the standard deviation of the energy of combustion of five acceptable experiments was 0.2 %. Unfortunately, however, the accuracy of these energies is in doubt, as the nickel and iron impurities subsequently found in the ThF_4 liner may have taken part in the combustion reactions or in the assay for unburned metal.

Thorium combustion experiments will be resumed when better techniques have been developed.

⁴⁷ ANL-6925, p. 179; ANL-6900, p. 227.

7. Potential Application of Nitrogen and Phosphorus Trifluorides in Calorimetry

(E. RUDZITIS, E. VAN DEVENTER)

NF₃ and PF₃ are gases which have interesting potentialities as calorimetric reagents. Despite their general similarity in physical properties (b.p., -121 and -101°C, respectively), their thermodynamic stabilities differ widely. The ΔH_f° values per gram-atom of fluorine are approximately -10 and -75 kcal, respectively. The further fluorination of PF₃ to PF₅ is accompanied by an energy change of -75 kcal per gram-atom of fluorine. Thus, the tendency of PF₃ to form PF₅ by liberation of ~150 kcal mol⁻¹ makes PF₃ a powerful fluorine stripping agent. Conversely, the low stability of NF₃ suggests its application as a mild fluorinating agent.

The potential value of NF₃ and PF₃ for calorimetric applications becomes further apparent when one considers the following: (1) both gases are relatively chemically inert; however, once activated (e.g., by a spark) they become quite reactive; (2) the products of the fluorination and defluorination (fluorine stripping) reactions are the gases N₂ and PF₅, respectively, and no stable intermediates are formed; (3) NF₃ and PF₃ are commercially available as compressed gases and can be readily purified; (4) accurate weighing techniques⁴⁸ have been developed for metering-in such gases; and (5) analytical procedures based on gas separations by fractional volatilization have been developed in this laboratory for analyzing these reactants and their products.

(a) *Thermochemistry of NF₃ and PF₃*. Prerequisite to the calorimetric utilization of NF₃ or PF₃ is the accurate knowledge of their enthalpies of formation. A literature review shows that the uncertainty associated with ΔH_f° (NF₃) is too large for a fundamental quantity and that the thermochemistry of PF₃ is even more unsatisfactory.

Two major compilers list $\Delta H_{f,298}^\circ$ (NF₃) = -30.4 ± 2.0⁴⁴ and -29.8⁴⁹ kcal mol⁻¹. These values were obtained from the evaluation of bomb calorimetric determinations based on the following reactions:

Reactions 4⁴⁸, 50, 51 and 5⁵¹ are directly or indirectly

⁴⁸ G. C. Sinke, J. Chem. Eng. Data **10**, 295 (1965).

⁴⁹ D. D. Wagman et al, National Bureau of Standards Technical Note 270-1, Washington, D. C., 1965.

⁵⁰ O. Ruff and H. Wallauer, Z. Anorg. Allgem. Chem. **196**, 421 (1931).

⁵¹ G. T. Armstrong, S. Marantz, and C. F. Coyle, J. Am. Chem. Soc. **81**, 3798 (1959).

affected by the uncertainties of the thermochemistry of HF; reaction 6⁵² has an associated uncertainty of ±1.2 kcal mol⁻¹ because of incomplete combustion of boron and related analytical problems.

The $\Delta H_{f,298}^\circ$ (PF₃) value has been quoted as -212 ± 10³⁴ and -219.6⁴⁹ kcal mol⁻¹; both values were derived from the early solution calorimetric work of Berthelot.⁵³ Another value, -221.95 kcal mol⁻¹,⁵⁴ is actually based on an estimated average bond energy of PF₃. A recent equilibrium study of the reaction

yielded ΔH_f° (PF₃) = -226.03 kcal mol⁻¹,⁵⁵ this value should have an appreciable uncertainty because of the uncertainties in the auxiliary ΔH_f° values, particularly that of CaF₂.

(b) *Proposed Determination of ΔH_f° (PF₃) and ΔH_f° (NF₃)*. Since an accurate $\Delta H_{f,298}^\circ$ (PF₅) value of -380.8 ± 0.3 kcal mol⁻¹ is already available,³⁵ the value for ΔH_f° (PF₃) can be derived by determining the enthalpy of the reaction

Trial combustions in a two-chambered reaction vessel with twofold to threefold excesses of fluorine have demonstrated the feasibility of carrying out reaction 8 with sufficient amounts of reactants to liberate 3 to 6 kcal of heat. Analysis of the combustion gases by fractional volatilization and infrared scan failed to detect any unreacted PF₃ (present detection limit, 0.1 v/o). The heat of mixing of PF₅ and fluorine can be directly determined by experiment.

The application⁵² of reaction 6 to the determination of ΔH_f° (NF₃) indicates that the fluorination of certain elements with NF₃ might be a promising approach to the determination of ΔH_f° (NF₃), particularly in view of the availability of accurate enthalpy-of-formation values and well-defined calorimetric specimens in this laboratory. Exploratory bomb combustion experiments with NF₃ indicated that the ease of combustion increased in the order B, Si, P and S. Some difficulties, however, became apparent: in order to avoid the formation of lower fluorides and/or the recovery of unburned sample, it was necessary to use an excess of NF₃, which

⁵² F. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data **8**, 76 (1963).

⁵³ M. Berthelot, Compt. Rend. **100**, 81 (1885).

⁵⁴ R. L. Porter and V. D. DiStefano, J. Phys. Chem. **65**, 849 (1961).

⁵⁵ H. C. Duus and D. P. Myxtyouk, J. Chem. Eng. Data **9**, 858 (1964).

caused local heating and a side reaction, namely, the partial decomposition of the excess NF_3 to its elements. None of these difficulties were encountered in a completely different approach in which NF_3 was mixed with excess PF_3 in a bomb. Upon ignition the reaction

proceeded explosively and completely.

(c) *Some Possible Applications of NF_3 and PF_3 in Fluorine Bomb Calorimetry.* The following paragraphs list some attractive applications of NF_3 and PF_3 reactions.

(1) The reaction of NF_3 with hydrogen in the presence of liquid HF or H_2O could be utilized for the determination of $\Delta H_f^\circ(\text{HF}, \ell)$ and $\Delta H_f^\circ(\text{HF}, \text{aq})$, thus bypassing the thermodynamic complexities of HF gas. The advantage of using NF_3 instead of fluorine is that NF_3 can be brought in contact with hydrogen or water without explosion or interaction, until triggered.

(2) NF_3 is known to react with hexafluoroethane according to the equation

The C—C bond energies in other fluorocarbons might be determined by similar reactions.

(3) Exploratory experiments have indicated that PF_3 reduces BrF_5 , SF_6 , and SF_4 . It seems likely that the PF_3 reduction of xenon fluorides could be used to determine their enthalpies of formation in the same fashion as that of NF_3 .

(4) A means of determining ΔH_f° values of intermediate metallic fluorides is exemplified by the reaction

(5) Another property of PF_3 which may also have potential calorimetric application is its tendency to react with O_2 and Cl_2 , leading to the formation of POF_3 and PCl_2F_3 , respectively.

The enthalpy of the reaction

is nearly $-70 \text{ kcal mol}^{-1}$.⁵⁶ There are no thermochemical data on PCl_2F_3 , but the reaction

was found to be essentially complete at room temperature.⁵⁷

In conclusion, it appears that an extensive calorimetry using NF_3 or PF_3 is both feasible and desirable and work along these lines will be continued.

8. The Enthalpy of Formation of Uranium Compounds (J. L. SETTLE)

The considerations leading to the construction of a fluorine flow calorimeter for determining the enthalpies of formation of fluorine-sensitive substances, e.g., uranium compounds, were discussed previously.⁵⁸ A fluorine flow calorimeter has been completely assembled and preliminary testing is in progress. Satisfactory combustions of uranium monosulfide in the flow system were obtained without encountering the problems associated with combustions in a bomb calorimeter.

Although the system was constructed primarily for the combustion of uranium compounds in fluorine, it may have application to other materials requiring careful regulation of the fluorine flowrate during the reaction period. Furthermore, the system can easily be modified to accommodate other gaseous reactants, such as those discussed in the previous section.

9. Quartz-Crystal Thermometry (E. GREENBERG)

A Dymec quartz-crystal thermometer has been fitted to a rotating bomb calorimeter (ANL-R2) and is being used together with a Hewlett-Packard 12-channel printer and an electronic timer to provide simultaneous automatic printout of time and temperature. The computer program for calculating the corrected temperature rise in a combustion experiment

has been modified to accept the automatic printout. Both the data-recording equipment and the computer program appear to have functioned satisfactorily when tested with a series of benzoic acid calibration runs.

⁵⁶ E. Ebel and E. Bretcher, *Helv. Chim. Acta* **12**, 450 (1929).

⁵⁷ J. N. Wilson, *J. Am. Chem. Soc.* **80**, 1338 (1958).

⁵⁸ ANL-6925, p. 182.

10. 1500°C Drop Calorimeter (J. E. BRUGGER, R. NORRIS,⁵⁹ R. BARNES⁶⁰)

Enthalpy increment data obtained for aluminum oxide (synthetic sapphire, National Bureau of Standards-Calorimetry Conference standard) and uranium monophosphide have been under study. A preliminary calculation for the alumina sample showed that the enthalpy differences, $H_T - H_{298}$, in the range studied, 1000 to 1400°K, agreed with those reported by the N.B.S. to better than 1%. A provisional value for the mean heat capacity of the uranium monophosphide sample in the range 800 to 1200°C is 13.8 cal deg⁻¹ mol⁻¹.

There still exist some uncertainties about the optimum manner of treatment of the data. The quantities measured are the temperature of the sample in the furnace before a drop and time *vs.* temperature of the copper-block calorimeter receiver before, during, and after a drop. Drops are made of both empty and filled sample capsules. As usual, it was assumed that the heat losses of empty and filled capsules at the same temperature were equal. The temperatures of the samples in the furnace were measured (1) with a Pt-10% Rh/Pt thermocouple embedded in the innermost furnace core element, and (2) by visual sightings into a black-body cavity in the capsule with an optical brightness pyrometer. Certain discrepancies between these sets of readings remain to be re-examined.

The method for determining the corrected temperature rise of the copper block after a hot drop is being improved. To determine the heat-leak correction to be applied to the observed temperature rise, use is made of the heat-leak constant, α (sec⁻¹), for the calorimeter. Among other factors, the value of α is inversely dependent on the heat capacity of the calorimeter. The change in heat capacity of the calorimeter with temperature (approx. 0.15% per °C) has an influence on

the energy equivalent of the calorimeter which can be accounted for by proper procedures. In addition, α is approximately ½% higher before a drop (when there is no capsule in the calorimeter) than after. Even after these effects are taken into account, there remain some vagaries in the results that appear to be larger than those assignable to the known uncertainties. It is suspected that moderate-term (½ hour) changes in ambient temperatures are influencing the results to a greater extent than had been predicted. Under certain circumstances, it may be possible to eliminate the suspected influence of ambient temperature changes by computational devices.

An alternative method, less laborious than the one in use, for determining the energy dissipated in the copper-block calorimeter during an electrical calibration has been devised and remains to be tested.

Some simple devices have been assembled to give a visual record of the position-*vs.*-time sequence of the capsule during its travel from the furnace to the calorimeter (nearly free fall, with strong deceleration near the end of the drop). This information is desirable for making accurate corrections of heat lost during a drop.

The task of bringing out the thermel and heater lead wires from the adiabatic calorimeter (now under construction to replace the copper-block calorimeter) is continuing. A few modifications are also being made to the drop tube and shutter drive assembly of the adiabatic calorimeter.

Because of the considerable experience which has now been gained in operation of the 1500°C drop calorimeter, it is anticipated that the accuracy and precision of future measurements will be markedly improved.

11. 2500°C Electron-Beam-Heated Calorimetric System (D. R. FREDRICKSON)

The calorimetric system⁶¹ for determining enthalpy increments to 2500°C is being tested with all components assembled except for the copper-block calorimeter, optical viewing port, and water-cooled shutter. Shop work is complete on copper-block calorimeter II and is progressing satisfactorily on the optical viewing port and water-cooled shutter.

The motorized target drive is illustrated in Figure III-10. The target drive, which operates in a vacuum,

consists of a 100-rpm motor attached via suitable gears to a hollow shaft. The shaft, in turn, is attached via a collet to the target and rotating shields. The furnace chamber is just below the target drive. When the latter is lowered, the target becomes the core of the furnace. Preliminary tests at elevated temperatures indicated mechanical interference between the rotating shields and the stationary spiral radiation shield which caused the motor to stall. To eliminate this trouble the outside diameter of the rotating shields was reduced and the shaft bearings were replaced with stainless steel, shielded, ball bearings having loose internal

⁵⁹ Student aide, Beloit College.

⁶⁰ Co-op student, University of Missouri.

⁶¹ ANL-7055, p. 175, Figure IV-1.

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Fig. III-10. Motorized Target Drive.

clearance. If the ball bearings are ineffective, an angular contact bearing or a sleeve-type nonmetallic bearing will be tested for this difficult service.

Figure III-11 is a drawing of copper-block calorimeter II with its associated optical viewing port and water-cooled shutter. The changes made from the design of copper-block calorimeter I⁶² provide for (a) a $\frac{3}{8}$ -in. thick shutter recessed in the block for better thermal equilibration, (b) the installation of a quartz-crystal thermometer, (c) faster calibration heating, and (d) faster cooling of the block between runs. Copper-block calorimeter II is still in the process of assembly. Meanwhile, a 9-in. length of nominal 1-in. dia. glass pipe with appropriate O-ring seals, brass flanges, and tie rods has been assembled for use as a test receiver for hot drops. Some drops have been made with a 1-cm dia. by 4-cm solid cylinder of tantalum heated to 900°C.

108-9616

Fig. III-11. Copper-Block Calorimeter II with Optical Viewing Port and Water-Cooled Shutter.

D. LIQUID SODIUM COOLANT CHEMISTRY (A. COSGAREA, JR., H. M. FEDER, M. ADER)

The chemistry of liquid sodium is being studied to obtain fundamental information on chemical reactions which may lead to corrosion and, therefore, affect the use of sodium as a heat transfer fluid in nuclear reac-

tors. The reactions of carbon-, nitrogen-, oxygen-, and hydrogen-bearing impurities in sodium are of especial interest in this connection. However, the present stud-

⁶² ANL-6800, p. 322.

ies have been restricted to the contaminant carbon and, in particular, to its characterization and removal.

The long-range objective of the program is the development of sufficient technical knowledge to understand and control mass-transfer and carburization-decarburization phenomena encountered in heat exchangers and fuel cans in contact with liquid sodium. The short-range objectives of the program are: (1) to develop reliable methods for the identification and determination of carbon species in sodium, (2) to characterize the products of reaction of typical carbon compounds with sodium at temperatures of practical interest, and (3) to develop methods for obtaining carbon-free sodium.

During the past two years, a reliable analytical method for the determination of total carbon in sodium has been developed. In addition, gas chromatographic analysis of gases evolved during reactions of

sodium and various solvents has yielded indirect information about the nature of some of the carbon-bearing species. Approximately 55% of the total carbon (~40 ppm) in United States Industrial Co. (U.S.I.) reactor-grade sodium has been accounted for by three products obtained on its dissolution in water: a trace of methane, equivalent to 0.7 to 1.6 ppm carbon; carbon dioxide, equivalent to about 6 ppm carbon, when the alkaline solution is acidified; and a filterable residue of finely divided, dark particles, equivalent to about 14 ppm carbon. This residue accounts for 30 to 70% of the total carbon typically found in sodium from various suppliers. Current studies are based on the hypothesis that the origin of these residues is the partial agglomeration of pre-existing, submicron-sized (possibly colloidal) particles of elemental carbon.

1. Physical Nature of Carbon in Sodium

a. CENTRIFUGATION EXPERIMENTS (C. LUNER, K. ANDERSON, J. ALLEN)

Previous experience has shown that particulate matter containing carbon is present in sodium and that these particles can pass through a 5 μ -porosity filter.⁶³ The feasibility of centrifugal segregation of particulate carbon in liquid sodium at 200°C was previously tested using forces of 300 to 625 g.⁶⁴ No significant segregation was found, which indicated that the carbon-containing particles were probably less than 1 μ in diameter. The use of larger centrifugal forces was recently tested with a 56 w/o Na-44 w/o K alloy. This alloy melts at 19°C, and was substituted for sodium because of the unavailability of a high-speed centrifuge capable of operation above the melting point (98°C) of sodium.

The alloy was sealed in stainless steel centrifuge tubes in a helium-atmosphere glovebox and (1) centrifuged at 17,000 rpm (~35,000 g) in a Sorvall Model RC-2 centrifuge for 40 min, then slowed to a stop over the next 20 min; or, (2) centrifuged at 40,000 rpm (~130,000 g) in a Spinco Model L Preparative Ultracentrifuge for 3¾ hr, of which the final 1½ hr was at 0°C in order to freeze the alloy while spinning. In both cases, the centrifuge tubes were tilted to the rotor axis (34° and 20°, respectively). After centrifugation, the tubes were cooled in liquid nitrogen and opened within the glovebox for sampling. Samples could not be taken from specific locations in the solid alloy be-

cause of its extreme brittleness. Therefore, the alloy was allowed to liquefy slowly and samples were withdrawn by pipette from the top of the liquid. The results of the carbon analyses were: before centrifugation, 76, 53, 36, 43 ppm; after centrifugation at 17,000 rpm, 22, 23 ppm; after centrifugation at 40,000 rpm, 23, 34 ppm. Statistical analysis of these data indicates that, at the 95% confidence level, there is a significant reduction in carbon content from the original to the centrifuged alloy. The separations obtained may not represent the maximum achievable: redistribution of carbon particles by convection and vibration could have occurred during the melting and sampling steps. A moderate-speed centrifuge (~17,000 rpm) has been purchased and will be modified to enable heating and, therefore, centrifugation of liquid sodium. Since sodium is solid at room temperature, redistribution of particles during sampling will not be a problem. Furthermore, solid sodium is not as brittle as Na-K alloys, and thus it will be possible to sample various portions of the solidified, centrifuged sodium.

b. ZONE MELTING (R. YONCO)

On the supposition that particulate carbon might be swept by a moving, solid-liquid, sodium interface, a test experiment was performed which utilized the zone-refining technique of repetitive, unidirectional, melt-freeze cycles.

About 25 g of filtered, reactor-grade sodium (~3 ppm carbon) was sealed under vacuum in 10-mm OL fused silica tubing. (The tube had been cleaned in hot dichromate cleaning solution, rinsed with distilled wa-

⁶³ ANL-6925, p. 92.

⁶⁴ ANL-7055, p. 84.

ter, sealed at the bottom, and vacuum-dried for one hour at 200°C and 10 microtorr.) The finished tube had an overall length of 24 in. and was filled to about 20 in. The tube was mounted vertically in a Fisher Zone Refiner and was heated by a resistance ring which moved downward over the length of the sodium column at 2.4 in./hr. The molten zone varied in length from ½ to 2 inches, the longest zones being located at the ends of the tube where heat conduction paths were minimized. The length and shape of the molten zone were difficult to determine because the sodium wet the fused silica and, hence, the solid-liquid interface was indistinct. After 240 heating cycles, the tube was scored with a file into 29 sections, each ~17 mm long, cleaned, and then transferred to a helium-atmosphere glovebox. There, the individual sections were broken off. With the aid of a special tool, each section could be grasped and a central core of solid sodium then extruded by the motion of a glass plunger. The extrusion process left an appreciable amount (as much as 15%) of sodium residue adhering to the tubing walls.

Analysis of the cores and the sodium residues for total carbon revealed the following. Carbon concentration in the cores decreased sharply at the upper end of the sodium column: from ~19 ppm at the top to

~9 ppm two inches below; cores from the middle and bottom sections contained only 3 to 4 ppm carbon. This vertical segregation, counter to the direction of zone travel, is not due to the concentration of a soluble species in the liquid phase. Unexpectedly, the sodium residues clinging to the silica sections were found to contain 5 to 10 times higher concentrations of carbon than the corresponding cores. Blank analyses of pieces of tubing showed negligible carbon contributions from the tubing; hence, it was concluded that the high concentration of carbon found in the residues was indicative of a real segregation of carbon toward the sodium-silica interface. When one of the bottom sections was sampled by melting the sodium out of its silica cylinder, rather than by extruding it, a carbon content of 5.6 ppm was obtained. This result suggests that the bulk of the carbon impurity remaining behind in the silica cylinder was strongly adsorbed at the silica-sodium interface rather than merely associated with the residual sodium. Further experiments are planned to elucidate the variables involved and the possible involvement of surface activity of particulate carbon. It should be noted that the sodium cores from the middle and bottom sections contained less carbon than any sodium previously analyzed in this laboratory.

2. Chemical Species in Sodium

a. HEXASODIUM HEXACARBONYL (C. LUNER, K. ANDERSON)

Previous mass spectrometric studies have indicated that stable organic compounds could exist in sodium.⁶⁵ If such compounds were present, their extraction by a hydrocarbon solvent would seem feasible. This concept was previously tested by repetitive extraction of reactor-grade sodium with high-purity n-nonane under a helium atmosphere at 125°C in a Pyrex glass vessel. None of the fractions showed any absorption between 2200 and 4000 Å.⁶⁶

The possibility remained that there are polar organic compounds in sodium which are not extracted by hydrocarbon solvents. Such compounds might simply dissolve in either alkaline or acid aqueous solutions without gas evolution and, hence, would not be detected by gas chromatography. An example would be the sodium salt of hexahydroxybenzene, otherwise called hexasodium hexacarbonyl, $\text{Na}_6(\text{CO})_6$, which is known to be a product of the reaction between sodium and carbon monoxide. Accordingly, U.S.I. sodium was dissolved in distilled water and the clear solution was

examined spectrophotometrically; dilute sodium hydroxide was used in the reference cell. No significant absorption was found in the ultraviolet and visible regions (2150 to 7000 Å), indicating that the sodium did not contain a significant amount of stable, sodium hydroxide-soluble, aromatic compounds. The sensitivity of detection was such that sodium hydroxide solutions containing hexahydroxybenzene equivalent to ~1 ppm of carbon in sodium would give discernible absorption peaks in the ultraviolet.

b. STABILITY AND SOLUBILITY OF SODIUM CYANIDE (C. LUNER, K. ANDERSON)

Cyanide is a potential carburizing agent in liquid sodium; hence, its behavior in liquid sodium is of some interest. Although not ordinarily present in as-received sodium, cyanide has been shown^{67, 68} to form readily in liquid sodium at elevated temperatures by reaction of carbon impurities, such as sodium carbonate, with nitrogen. An investigation of the solubility and stability of sodium cyanide in liquid sodium is being undertaken since so little is known about its behavior.

⁶⁵ ANL-7125, p. 140; ANL-7055, p. 85.

⁶⁶ ANL-7055, p. 86.

⁶⁷ E. W. Hobart and R. G. Bjork, Nucl. Appl. 1, 490 (1965).

⁶⁸ ANL-7125, p. 141.

In preparation for the solubility work, the stability of NaCN (m.p. 564°C) was examined. Sodium cyanide was held at 600°C for 64 hr in the presence and absence of sodium in containers made of 316 SS, tantalum, or fused silica. The products were dissolved in water and analyzed for cyanide content by titration with AgNO₃. Cyanide recoveries ranged from 85 to 95%, with no apparent effect of the container material. The appar-

ently incomplete recoveries may have resulted from interference by impurities with the titration.

Preliminary results have indicated a rather low solubility (<100 ppm) of NaCN in sodium between 180 and 530°C. Therefore, Na¹⁴CN is being prepared for the solubility study, and a radiochemical procedure for analysis of carbon-14 is being developed.

3. Ultrapurification of Sodium (R. HEINRICH)

The commercial manufacture of sodium by high-temperature electrolysis of NaCl-CaCl₂ mixtures employs graphite anodes and metal cathodes. The anodes are gradually eroded during the electrolysis and small particles of graphite, not completely removed by subsequent processing, are found in the sodium. Because it is desirable that small quantities of pure sodium be available for analytical development work and for reaction studies, electrolysis of 60 m/o NaCl-CaCl₂

with nickel or tungsten anodes was attempted on a laboratory scale.

To date, five laboratory-scale electrolytic cells have been set up and operated. Each has failed to produce recoverable amounts of sodium. The difficulties encountered were directly attributable to the miniaturization of the commercial design. Since the process does not appear to be readily scaled down, this effort is being suspended and other approaches to the purification of sodium will be considered.

E. CHEMISTRY OF LIQUID METALS (H. M. FEDER, M. ADER)

The chemistry of liquid metals and alloys is being investigated to provide basic data for the development and testing of theories of the metallic liquid state. Toward this goal the following experimental studies contribute in various ways.

Thermodynamic properties of liquid binary alkali metal solutions are being determined by atomic absorption spectrophotometry. The electronic structures of the alkali metals are believed to be simple and well known; hence, these data will provide tests for theories of the simplest metallic solutions.

An apparatus has been developed for the measurement of velocity and absorption of high-frequency sound in liquid metals. It is hoped that unambiguous evidence will be obtained for the existence or nonexistence of distinct atomic complexes in liquid alloys.

The existence of an intermetallic compound in the gaseous state would be a clue to its possible existence as a distinct species in the liquid state. The gaseous molecule HgK₃ had been postulated to exist in order to explain the vapor pressure behavior of potassium amalgams. A mass spectrometric search for it was made.

Small variations in the atomic radius ratios of pairs of metal atoms are known to have strong effects on their interactions in both the liquid and solid states. A systematic investigation of the zinc-rich phases in the zinc-rare earth alloy systems has been completed; the influence of atomic size is particularly evident in the results.

1. Thermodynamic Properties of Liquid Binary Alkali Metal Solutions (F. CAFASSO, L. JONES)

Recent advances⁶⁹ in theoretical methods for treating properties of metallic solutions have indicated a need for experimental data on simple metallic systems to test

these methods. The alkali metals form simple binary solutions which should lend themselves to theoretical treatment.⁷⁰ Accordingly, we are determining thermo-

⁶⁹ A. Bellemans and M. DeLeener, *Phys. Rev. Letters* **6**, 603 (1961); *Phys. Letters* **4**, 157 (1963).

⁷⁰ J. R. Christman and H. B. Huntington, *Phys. Rev.* **139**, A83 (1965).

TABLE III-6. COMPARISON OF OBSERVED AND CALCULATED PRESSURES OF MONATOMIC POTASSIUM

Temp ^a (°K)	<i>I/I</i> ₀	Pressure × 10 ⁹ (atm)		
		<i>Pα</i> (obs.)	Ref. 77	Ref. 78
341.9	0.284	1.62	1.83	1.79
342.6	0.259	1.74	1.94	1.90
343.2	0.255	1.77	2.05	2.01
344.6	0.216	1.99	2.33	2.28
345.5	0.203	2.08	2.52	2.47

^a The actual sequence of temperatures was random.

dynamic activities of selected alkali metals in their binary liquid solutions.

The experimental method is based on the principles of atomic absorption spectrophotometry⁷¹ and has been shown to be highly effective for the determination of the thermodynamic activities of both sodium and potassium in their binary solutions.⁷² These activities were determined by comparing the absorption of resonance radiation (5890 Å sodium or 7665 Å potassium lines) by vapor above Na-K solutions with that above pure sodium or pure potassium. The absolute values of the partial pressures of sodium and potassium can also be obtained from vapor absorption measurements for pure liquids. The experimental data obtained for pure sodium were previously examined⁷³ in terms of absolute pressures and were shown to be in good agreement with literature-based values. The data for pure potassium are treated similarly below.

Equation 1 relates the transmission of the 7665 Å potassium line to the pressure of monatomic potassium. This equation includes terms⁷⁴ due to the Doppler

breadth and the nuclear hyperfine structure⁷⁵ of the 7665 Å line.

$$I/I_0 = \frac{3}{8} \exp(-0.6366 \ell K_0) + \frac{5}{8} \exp(-0.7793 \ell K_0) \quad (1)$$

where

$K_0 = (2.680 \times 10^{12} P\alpha)/T^{3/2}$, the constant being based on a value of 0.66 for the oscillator strength,⁷⁶

P = partial pressure of monatomic potassium, atm,

T = absolute temperature, °K,

ℓ = optical path length (2.54 cm),

α = emission line width factor.

The partial pressures of monatomic potassium determined from some representative absorption measurements for pure potassium at about 70°C are shown in Table III-6 and compared with values based on equations developed by Thorn and Winslow⁷⁷ and by Nesmayanov.⁷⁸ The observed values, if α were equal to unity, would be consistently lower than the literature-based values by about 8 to 18 %. The correct value of α is difficult to determine without a high-resolution scan of the profile of the 7665 Å line, but by a method outlined by Mitchell and Zemansky⁷⁹ and Vidale,⁸⁰ a value of 0.80 to 0.85 can be estimated. The observed values would accordingly increase by 15 to 20 %. Since there is an uncertainty of about 10 % in the literature-based values, it is concluded that substantial agreement exists between the observed and calculated pressures for potassium.

The activities of rubidium and cesium in Rb-Cs solutions will be investigated next.

2. Ultrasonic Measurements in Liquid Metals (F. CAFASSO, R. BLOMQUIST)

Ultrasonic methods have come into prominence in recent years as a means for detecting complex species in

⁷¹ ANL-6725, p. 107.

⁷² ANL-6925, p. 95; ANL-7055, p. 80.

⁷³ ANL-7125, pp. 144-145.

⁷⁴ The factors which influence the relationship between pressure and transmittance are discussed in Ref. 5. Of these factors, only the Doppler breadth and nuclear hyperfine structure of the 7665 Å potassium line are significant here.

⁷⁵ Potassium has three natural isotopes: ³⁹K (93.08%), ⁴⁰K (0.01%), and ⁴¹K (6.91%). The nuclear hyperfine structure of the 7665 Å line was assumed to be due to the nuclear spin of ³⁹K only. The abundances and nuclear hyperfine splitting constants of ⁴⁰K and ⁴¹K are considerably smaller and, therefore, may be neglected in Eq. 1.

⁷⁶ G. Stephenson, Proc. Roy. Soc. (London) **A64**, 458 (1951).

⁷⁷ R. J. Thorn and G. H. Winslow, J. Phys. Chem. **65**, 1297 (1961).

⁷⁸ A. N. Nesmayanov, "Vapor Pressure of the Elements," Academic Press, N. Y., 1963, p. 443.

nonmetallic solutions.⁸¹⁻⁸⁴ The potential of these methods with regard to the detection of association in metallic solutions, however, has not yet been fully explored. For example, the method of continuous variations

⁷⁹ A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London, 1961, p. 122.

⁸⁰ G. L. Vidale, "The Measurement of the Vapor Pressure of Atomic Species from Spectrophotometric Measurements of the Absorption of Resonance Lines," Gen. Elec. Co., Phila., Pa., T.I.S. Report R60SD330, May, 1960.

⁸¹ J. R. Saraf and P. N. Sharma, J. Sci. Res. Inst. (Tokyo) **49**, 236 (1955).

⁸² P. C. Bose and L. N. Srivastava, Z. physik. Chem. (Leipzig) **205**, 96 (1955).

⁸³ T. Satyavate, P. J. Reddy, and S. V. Subrahmanyam, J. Phys. Soc. Japan **17**, 1061 (1962).

⁸⁴ S. Prakash, F. M. Ichhaporia, and J. D. Panday, J. Phys. Chem. **68**, 3078 (1964).

FIG. III-12. Apparatus for the Measurement of Ultrasonic Velocity in Liquid Metal Solutions.

(method of Job⁸⁵) has been used successfully with ultrasonic velocity measurements to show the formation of aqueous complexes¹⁶ but has not been tried with liquid metals. We are planning to search for association in liquid metals by using the method of continuous variations in conjunction with ultrasonic velocity measurements.

Ultrasonic velocity measurements are being made by the pulse-echo method. This method involves the measurement of the time of transit of a short train of acoustic waves over a predetermined path length in a specimen material. Figure III-12 shows a schematic diagram of the acoustic apparatus being used for such measurements with liquid metals. This apparatus has two basic parts: a furnace chamber and an assembly consisting of a transducer attached to a fused-silica buffer rod. The furnace chamber is a flanged, closed-bottom, stainless steel tube, 14 $\frac{3}{4}$ in. long with an internal diameter of 3 $\frac{1}{4}$ in. It is made vacuum-tight with an O-ring-sealed,

water-cooled cover. The cover is provided with a valved port for evacuation, and with Wilson-type seals for the passage of an alumina thermocouple protection tube and the buffer rod. Three levelling screws, which pass through the cover and flange, support the chamber on a platform suspended above a Marshall furnace. The melt is contained in a primary quartz crucible⁸⁶ whose inside bottom is ground and lapped flat to 0.001 in. to serve as a reflector surface. The melt crucible and a secondary steel crucible are positioned in a uniform temperature zone of the furnace by a pedestal which fits into the bottom of the furnace chamber.

The transducer (5-Mc, X-cut quartz crystal) is $\frac{3}{4}$ in. in diameter and is bonded⁸⁷ to one end of a fused silica rod, 15 in. long by $\frac{3}{4}$ in. in diameter, whose bottom end is polished and lapped optically flat. The rod is coupled

⁸⁶ Either alumina or tantalum crucibles will be used with liquids which are corrosive to quartz.

⁸⁷ Nonaq stopcock grease (Fisher Scientific Co.) was used as the bonding agent in the present experiments.

⁸⁵ P. Job, *Ann. Chem. (Paris)* [10], **9**, 113 (1928).

to a shaft and a mechanical slide assembly. Vertical motion of the rod is accomplished by movement of the mechanical slide. The bottom of the buffer rod and the bottom of the crucible are made parallel by tilting the furnace chamber with the levelling screws. The furnace chamber is decoupled mechanically from the transducer, buffer-rod assembly by a bellows.

The transducer is driven by short electrical pulses from a pulsed RF oscillator.⁸⁸ The sound pulse so generated travels down the buffer rod through the liquid metal to the reflector face of the crucible, where it is reflected back to the transducer which is now quiescent. The transducer transforms the reflected acoustic pulse into an electrical pulse that is amplified and displayed on the screen of a cathode-ray oscilloscope along with

the initial pulse. A time-calibrated sweep is used to measure the time between the initial and reflected signals.

The velocities of sound in distilled water and in mercury were measured to test the reliability of this apparatus. Velocities of 1499.9 and 1448.7 m/sec were obtained for water (25°C) and mercury (24°C), respectively.⁸⁹ These velocities agree to within at least 0.1 % with the values of 1498.1 and 1449.2, respectively, reported by Hubbard and Loomis.⁹⁰ This agreement indicates that the instrument is dependable for the measurement of velocities in liquids at room temperature. To test its performance at elevated temperatures, the velocity of sound in liquid cadmium will be measured.

3. Vapor Species in the Potassium-Mercury System (E. VELECKIS, J. W. REISHUS,⁹¹

I. JOHNSON⁹²)

An interest in the vapor species over potassium amalgams developed when it became necessary to compute the thermodynamic properties of such amalgams beyond the temperature range of direct measurement. The thermodynamic properties were needed for calculating the efficiency of magnetohydrodynamic cycles in which potassium amalgams are employed as the working fluids.

At high pressures, the vapors of alkali metals contain an abundance of polymeric species which must be considered in the determination of the properties of the vapor. There are two extreme approximations which can be made. (1) The vapor can be considered as a monatomic assembly of atoms with all the apparent imperfections represented by terms in the virial equation of state. (2) The vapor may be considered as a mixture of ideal molecular species in which all imperfections are ascribed to association. The latter approach has been adopted by previous investigators in explaining the apparent nonideality of the vapors over potassium amalgams.

In 1929 Barratt⁹³ detected in the vapors over alkali metal amalgams band spectra which differed from those of pure alkali metals and which were, therefore, assigned to alkali metal-mercury compounds. A few years later Pedder and Barratt⁹⁴ measured vapor pres-

sures over potassium amalgams and deduced that a compound, probably HgK, existed in the vapor. However, Lumsden⁹⁵ pointed out thermodynamic inconsistencies in their argument. Roeder and Morawietz⁹⁶ measured the total vapor pressure over potassium amalgams with a quartz-spiral manometer and also determined the molecular weights of the vapors by the torsion-effusion method. They explained their experimental data by postulating a molecular vapor species, HgK₃, in addition to gaseous Hg and K. Ewing et al⁹⁷ investigated the P-V-T relations of pure potassium and found that the behavior of potassium vapor could be described by a mixture of K, K₂, and K₃ species, each behaving ideally. The most recent total pressure and emf cell study of potassium amalgams is that of LaMantia.⁹⁸ The practice of postulating a number of ideally behaving species to explain thermodynamic data does not in itself constitute proof of the existence of these species. To determine qualitatively the composition of the vapor over potassium amalgams, a mass spectrometric experiment was carried out.

Approximately 2 g of an amalgam containing 75 a/o potassium was prepared by mixing the component metals slightly above the melting point of the amalgam (~117°C) in an inert-atmosphere glovebox. This composition was chosen because the partial pressure of

⁸⁸ This oscillator is part of the ultrasonic attenuation comparator marketed by Sperry Products, Danbury, Conn.

⁸⁹ The liquids were contained in a quartz crucible for these measurements.

⁹⁰ J. C. Hubbard and A. L. Loomis, *Phil. Mag.* **5**, 1177 (1928).

⁹¹ High Temperature Materials Development Group.

⁹² Pyrochemical Research Group.

⁹³ S. Barratt, *Trans. Faraday Soc.* **25**, 758 (1929).

⁹⁴ J. S. Pedder and S. Barratt, *J. Chem. Soc.* **537** (1933).

⁹⁵ J. Lumsden, "Thermodynamics of Alloys," *The Institute of Metals*, London, 1952, p. 278.

⁹⁶ A. Roeder and W. Morawietz, *Z. Elektrochemie* **60**, 431 (1956).

⁹⁷ C. T. Ewing et al, "High-Temperature Properties of Sodium and Potassium," *NRL Report 6094*, U.S. Naval Research Laboratory, Washington, D. C., June 9, 1964.

⁹⁸ C. R. LaMantia, Ph.D. Thesis, Columbia University, 1965.

HgK_3 should be a maximum at this composition. The amalgam was placed in a Vycor thimble which, in turn, was placed in a tungsten Knudsen effusion cell. The instrument used for the analysis was a Bendix TOF mass spectrometer with a resolution of one in 200 and a sensitivity of 10^{-9} atm. Vapor species observations were made with ionizing electron energies of 10 and 20 eV, with the amalgam at approximately 200°C.

Shutter profile studies indicated that the major species vaporizing from the cell were K, K_2 and Hg. There was no evidence of K_3^+ , HgK^+ , HgK_2^+ , HgK_3^+ , or heavier ion species. At 20 eV the relative ion intensities (in arbitrary units) of the three parent species I_{K}^+ , $I_{\text{K}_2}^+$, and I_{Hg}^+ were 400, 0.26, and 40, respectively; the corresponding ratios, $I_{\text{Hg}}^+/I_{\text{K}}^+$ and $I_{\text{K}_2}^+/I_{\text{K}}^+$, are 0.1 and 6.5×10^{-4} , respectively. In contrast, Roeder and Morawietz⁹⁶ calculated partial pressures over a 77.5 a/o potassium amalgam at 200°C of 6.00×10^{-3} , 2.60×10^{-3} , and 1.62×10^{-3} torr for K, Hg, and HgK_3 , respectively; the corresponding ratios of $P_{\text{Hg}}/P_{\text{K}}$ and $P_{\text{HgK}_3}/P_{\text{K}}$ are 0.43 and 0.27, respectively.

Although HgK_3 was not observed, the possibility arises that perhaps the molecule exists in the vapor but has such a low dissociation energy that it can not be observed with a mass spectrometer. This question can be qualitatively answered by considering the gaseous K_2 and Hg_2 molecules. Even though the K_2 molecule has a low dissociation energy of 0.51 eV,⁹⁹ it was easily observed with the mass spectrometer. If the HgK_3 mole-

cule had a dissociation energy of approximately 0.5 eV, and were present in the vapor to the extent proposed by Roeder and Morawietz, it probably would have been detected. The Hg_2 molecule, with a dissociation energy of 0.06 eV,¹⁰⁰ was not observed. The partial pressure expected for Hg_2 under the experimental conditions was calculated to be 1.3×10^{-9} atm. Even though this pressure is very near the limit of detection of the mass spectrometer, it is believed that the Hg_2^+ ion, if present, would have been observed because of the very low background in the region of mass 400. If the dissociation energy of HgK_3 is similarly low, one would not expect to observe HgK_3 even if it were present in the vapor to a considerable extent. However, one might reasonably expect to see one or more of the fragment species K_3^+ , HgK^+ , or HgK_2^+ —none of which were observed. Roeder and Morawietz,⁹⁶ moreover, calculated an enthalpy of formation for gaseous HgK_3 of 65 kcal/mole, which would correspond to a dissociation energy of 2.8 eV. A dissociation energy of this order of magnitude would certainly render HgK_3 observable with the mass spectrometer unless, of course, its concentration was below the spectrometer's limit of detection.

The results of this experiment, therefore, indicate that the vapor phase over potassium amalgams consists of K, K_2 , and Hg. The species HgK_3 and K_3 apparently either do not exist or, at most, are very minor components of the vapor.

4. Crystal Structure of the Zinc-Rich Phases in Lanthanum-Zinc Systems

(E. VELECKIS, R. V. SCHABLASKE,¹⁰¹ B. S. TANI¹⁰¹)

The effects of small changes in atomic radius ratio on the stabilities of intermetallic phases are currently of great interest to metallurgists. Binary intermetallic phases formed by the rare earths (lanthanons) with some common partner offer an excellent opportunity for isolating the effects of size (the lanthanide contraction) from those of valency and electronegativity. Our previous effusion and X-ray diffraction studies¹⁰² of intermediate phases formed by zinc with lanthanum, cerium, praseodymium, neodymium, or yttrium showed that the zinc-rich phases undergo certain stoichiometric and structural changes which could be correlated with

the size of the lanthanon. In the present study the zinc-rich phases of the remaining lanthanons (with the exception of promethium) were examined by means of X-ray diffraction.

To prepare an alloy, weighed amounts of zinc and rare earths, corresponding to an alloy approximately 93 a/o in zinc, were sealed in a tantalum capsule by arc welding in an inert-atmosphere box. The alloy was heated at 600°C¹⁰³ for seven days and cooled slowly to room temperature. The resulting ingot was pulverized and screened in an inert atmosphere, and the powder passing through a No. 200 sieve was used to fill X-ray capillaries. X-ray powder diffraction patterns were made at room temperature with a 114.6-mm Debye-Scherrer camera with filtered $\text{CuK}\alpha$ radiation; filtered $\text{CrK}\alpha$ radiation was used with some alloys to achieve optimum resolution of the diffraction lines. Lattice

⁹⁹ G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand, Princeton, 1950, p. 543.

¹⁰⁰ A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London, 1953, p. 226.

¹⁰¹ Analytical Research and Development Group.

¹⁰² E. Veleckis, R. V. Schablaske, I. Johnson, and H. M. Feder, Trans. Met. Soc. AIME 239, 58 (1967).

¹⁰³ YbZn_{13} and the low-temperature modification of SmZn_{12} were prepared by heating at 475°C.

TABLE III-7. CRYSTALLOGRAPHIC PROPERTIES OF ZINC-RICH PHASES IN LANTHANON-ZINC SYSTEMS

Compound	Structure Type	C.N.	Lattice Parameters (Å)		Molar Volume (Å ³) ^a	Radius of Hole ^b for Ln Atom (Å)
			<i>a</i>	<i>c</i>		
EuZn ₁₃	NaZn ₁₃	24	12.212	—	228	2.16
YbZn ₁₃			12.160	—	225	2.15
LaZn ₁₃			12.088 ^c	—	221	2.12
EuZn ₁₁	BaCd ₁₁	22	10.716	6.875	197	2.07
LaZn ₁₁			10.68 ^d	6.87 ^d	196	2.07
CeZn ₁₁			10.66 ^d	6.86 ^d	195	2.06
YbZn ₁₁			10.663	6.822	194	2.05
PrZn ₁₁			10.65 ^d	6.85 ^d	194	2.05
NdZn ₁₁			10.635 ^c	6.839 ^c	194	2.05
NdZn ₁₂	UZn ₁₂	20	8.991	8.949	209	1.96
SmZn ₁₂ (h) ^e			8.972	8.912	207	1.95
SmZn ₁₂ (ℓ) ^e	ThMn ₁₂	20	8.923	5.203	207	1.94
GdZn ₁₂			8.903	5.207	206	1.93
TbZn ₁₂			8.889	5.203	206	1.93
YZn ₁₂			8.879 ^d	5.201 ^d	205	1.93
DyZn ₁₂			8.877	5.200	205	1.93
HoZn ₁₂			8.870	5.195	204	1.92
ErZn ₁₂			8.862	5.195	204	1.92
TmZn ₁₂			8.852	5.190	203	1.92
LuZn ₁₂			8.846	5.187	203	1.91

^a Calculated on the basis of 8 formula weights per unit cell for NaZn₁₃-type, 4 for BaCd₁₁-type, 3 for UZn₁₂-type, and 2 for ThMn₁₂-type compounds.

^b Calculated by subtracting Zn radius (1.38 Å for twelvefold coordination) from weighted average of Ln-Zn interatomic distances.

TABLE III-7—continued

^c Ref. 102.

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

^e (h) and (ℓ) denote high- and low-temperature modifications.

parameters were refined by a computer-programmed least-squares treatment.¹⁰⁴

The results are shown in Table III-7. The zinc-rich compounds crystallized in one, and in a few examples, two of the following structural types: face-centered cubic NaZn₁₃ (polyhedral coordination number, C.N. = 24), body-centered tetragonal BaCd₁₁ (C.N. = 22), hexagonal UZn₁₂ (C.N. = 20), body-centered tetragonal ThMn₁₂ (C.N. = 20). In each of these structures, the central atom is surrounded by a "cage" of 24, 22, or 20 approximately equidistant ($\pm 5\%$) zinc atoms. The cage may be considered as defining a hole in which a lanthanum atom resides. The radius of the hole can be estimated by subtracting the radius of a zinc atom (1.38 Å for twelvefold coordination) from the average Ln-Zn interatomic distance in the compound. In Table III-7, the phases are listed according to the sizes of the holes provided for the lanthanum atom, and subdivided into groups according to structure type. As expected, phases with higher coordination numbers also provide larger holes for the central atom, and within each group the order parallels the lanthanide contraction.

¹⁰⁴ M. H. Mueller and L. R. Heaton, "Determination of Lattice Parameters with the Aid of a Computer," ANL-6176, 1961.

IV

Reactor Safety¹

(R. O. Ivins, A. D. Tevebaugh, J. D. Bingle)

The program on reactor safety is concentrated in two areas of research: (1) the study of metal-water reactions, and (2) studies relating to the safety of fast reactors.

In water-cooled reactors, coolant failure or a severe nuclear excursion could cause the reactor core metals to melt and disperse rapidly in the water. Chemical reactions between the metals and water could result in the release of energy approaching or exceeding the energy released by the fission process during a nuclear excursion. Studies of these reactions are being carried out so that realistic estimates can be made of the rates and extents of reactions during hypothetical reactor accidents.

The reactions of the metals of interest with water are being studied in several ways. Experimental methods include isothermal reaction rate determinations, nonisothermal studies of the reactions with fine metal particles, in-pile meltdown experiments with specimens of typical reactor fuel materials, and heating experiments designed to simulate the conditions experienced by fuel elements during a loss-of-coolant

accident. An additional research area consists of calculational studies in which experimental results obtained by several methods are correlated and methods of accident analysis are developed.

In sodium-cooled systems (fast reactors), coolant failure or a severe nuclear excursion could cause melting and rapid dispersion of reactor materials in the sodium. To assess these and other potential problem areas, the following studies relating to the safety of fast reactors are being carried out: (1) chemical and physical interactions of fuel and cladding materials with liquid sodium, (2) transient heat transfer associated with any such interaction, (3) high temperature physical properties of fast reactor materials, (4) fuel migration and segregation in mixed uranium-plutonium compounds, and (5) reaction of sodium with air.

In addition, previous efforts in the field of metal oxidation and ignition kinetics have been extended in a brief study of the combustion characteristics of U-Pu-Mo and U-Pu-Ti ternary alloys.

A. METAL-WATER REACTIONS

1. Reaction of Flowing Steam with Stainless Steel-Clad and Zircaloy-2-Clad, UO₂-Core Simulated Fuel Elements (R. E. WILSON, C. BARNES)

Experiments designed to simulate the environment of the fuel in a water-cooled power reactor following a loss-of-coolant accident have continued. In such a situation, the fuel would be subjected to a slowly rising temperature as a result of the heat generated by fission product decay. Typical accident calculations (ANL-6925, p. 215 and ANL-7055, p. 192) have indicated that, in the absence of effective countermeas-

ures, average fuel temperatures would reach the melting point of the metal cladding in about 10 min.

The experiments were performed in the high-pressure furnace that has been previously described (ANL-6900, p. 242 and ANL-6925, p. 187). The furnace is contained within a steel pressure vessel and consists of two zones: an internal steam-filled zone that is surrounded by an alumina tube, and an external zone that is argon-filled. The argon-filled zone

¹ A summary of this section is given on pages 14 to 18.

ntains molybdenum heater windings and insulation. The pressures in the two zones are automatically matched to avoid stresses on the alumina tube. Water is introduced into the lower part of the steam zone by a positive-displacement pump and is converted to steam. At the start of an experiment, the sample is elevated from a moderate-temperature section, where reaction with steam is negligible, into the high-temperature section. The rate of elevation is controlled to simulate the temperature rise from decay heating. Some unreacted steam and the hydrogen produced by the metal-steam reaction are continuously removed from the upper part of the steam zone (high-temperature section) through an outlet valve. The extent and the rate of metal-steam reaction are determined by continuously monitoring the amount of

hydrogen collected. Upon completion of an experiment, the sample is rapidly lowered to its initial position.

Previously (see ANL-7125, p. 153), studies were made of the reaction of high temperature steam with single Zircaloy-2-clad and type 304 stainless steel-clad, UO_2 -core simulated fuel elements (8-in. long by $\frac{3}{8}$ -in. dia. rods, 0.025-in. cladding thickness). These studies have been extended to include bundles of 4 such rods. In the previous experiments, the fuel rod was held in the lower part of the furnace, with the top of the rod at a temperature of about 900°C . At the start of an experiment the fuel rod was raised at the rate of 1 in./min (total of 8 in.) until the upper part of the rod was in the hot zone (1500°C). After insertion, the fuel rod was held in the hot zone for 2 min and then rapidly removed. The results of these single-

08-9704A

FIG. IV-1. Four-Rod Bundle of Type 304 Stainless Steel-Clad, UO_2 -Core Fuel after Exposure to One Atm Steam at 1600°C . (Unexposed fuel rod also shown for comparison.)

108-9705A

FIG. IV-2. Close-up View of the Four-Rod Bundle of Type 304 Stainless Steel-clad, UO_2 -Core Fuel Shown in Figure IV-1.

108-9257A T-1

FIG. IV-3. Four-Rod Bundle of Zircaloy-2-Clad, UO_2 -Core Fuel after Exposure to One Atm Steam at Temperatures Greater Than 1700°C . (Unexposed fuel rod also shown for comparison.)

rod experiments showed that the fuel rod surface temperature rose to about 1600°C (100°C above the furnace temperature) at the hot end for both types of cladding. Under these conditions the stainless steel cladding reacted about twice as fast as the Zircaloy-2 cladding.

In the present experiments, a 4-rod fuel bundle in a square array with 0.6-in. center-to-center spacing was exposed to 1 atm steam. The steam flow was increased from 10 g/min (the rate for the experiments with single elements) to 25 g/min to insure that the reaction was not steam-limited. Other experimental conditions were not altered from those used in the earlier experiments.

A 4-rod bundle (type 304 stainless steel cladding) that was exposed to high temperature steam is shown in Figure IV-1. The holder is shown at the bottom and an unexposed fuel rod on the right. Figure IV-2 is a close-up view showing the area near the boundary (which was at a temperature of about 1400°C) between the rapid "frothing" reaction and the slow "corrosion" reaction. In the area of rapid reaction, the expansion of the reaction products into the steam flow channel is evident, with bridging between fuel rods occurring in some areas. The amount of hydrogen evolved per rod was about the same as that observed in similar experiments with single fuel rods (i.e., the total amount of hydrogen evolved was approximately four times the amount evolved in the experiments with single rods).

A 4-rod bundle (Zircaloy-2 cladding) is shown in Figure IV-3 after exposure to high temperature steam, along with an unexposed rod. The holder is at the left. Although the fuel rods were badly damaged, a large portion of the fuel was still encased in tubes of oxidized Zircaloy. Some of the damage to the cladding occurred while the test section was being removed from the furnace. Self-heating of the Zircaloy-2-clad rods was apparent; during the run the temperature of the hot end of the sample exceeded 1700°C (more than 200°C above the furnace temperature). The hydrogen evolved per fuel rod was about twice that observed in the single-rod experiment, which would be expected because of the higher temperatures reached by the 4-rod bundle.

The additional self-heating of the Zircaloy-2 cladding due to thermal isolation in the 4-rod bundle points up the need for further studies with large numbers of rods. This topic is discussed more fully in the following section (IV.A.2.).

2. Large-scale Simulations of the Loss-of-Coolant Accident (R. O. IVINS, R. E. WILSON, J. C. HESSON, T. W. ECKELS²)

The conditions of experiments (such as those described in the preceding section) that were performed in the high pressure furnace to simulate the environment following a loss-of-coolant accident were limited by the capabilities of the furnace. Experiments were conducted at temperatures only as high as 1700°C; at that temperature melting of the Zircaloy-2 cladding is not achieved (zirconium m.p., 1852°C). In addition, the furnace is only capable of handling bundles of four 8-in. rods. In order to simulate adequately the conditions following a loss of coolant, it is desirable to heat larger bundles and to achieve much higher temperatures.

In a following section (IV.A.6.) of this report, an experiment is described in which a bundle of 3 rods was heated rapidly (12 sec) in the TREAT reactor to temperatures sufficient to melt the UO₂ core of the rods. This technique allows high temperatures to be reached, but does not adequately reproduce the conditions following a loss of coolant. High temperatures can be sustained in TREAT only for very short times of the order of 10 sec, rather than the several hundred seconds necessary to duplicate the loss-of-coolant situation.

The Division of Reactor Development and Technology, U.S. Atomic Energy Commission, requested that a study be made to evaluate the possibilities of conducting large-scale loss-of-coolant simulations by both laboratory and in-pile techniques. During the past half-year, a considerable effort was made to obtain the requested information. The proposed objectives of the experiments are (1) to test calculational models (such as those described in Section IV.A.3. of this report) and (2) to obtain the information necessary to develop calculational models that will describe the collapse of the core as melting temperatures of cladding, cladding oxide, and fuel are reached, and

will characterize the metal-steam reactions occurring during this phase of the accident.

In these evaluations, it was proposed that bundles of nineteen fuel elements (each 3-ft long by ~0.4-in. dia., in a hexagonal array) be heated in flowing steam or steam-air mixtures. This would represent a full-scale section of the LOFT (Loss of Fluid Test) reactor core.³

The laboratory experiments would allow a study of the events that happen following a loss of coolant until cladding failure occurred. In these experiments, tungsten rods (shaped to achieve an axial cosine power distribution) would be placed in the axial center of the UO₂ pellets. These rods would be used as resistance heaters to achieve temperatures sufficient to melt Zircaloy-2 cladding. It is expected that shortly after the fuel element cladding failed, the tungsten heater rods would also fail as a result of reaction with steam. However, prior to failure of the heater rods, the cladding-steam (and -air) reaction could be determined under closely controlled conditions, and compared with the calculational models.

To develop calculational models that would adequately describe the core collapse, the performance of in-pile experiments would also be necessary. Using fission heating to simulate decay heating, temperatures sufficient to melt both UO₂ and the cladding could be achieved on time scales representative of the conditions after a loss of coolant. As a result of the evaluations, it was concluded that experiments of this type could be accomplished in presently available reactor facilities, although considerable modifications of these facilities might be necessary.

The evaluations described above, which also included preliminary cost estimates and schedules, were completed during this half-year period and submitted to the Division of Reactor Development and Technology, USAEC, for their consideration.

3. Calculation of the Extent of Metal-Water Reaction During a Loss-of-Coolant Accident (CHEMLOC Program) (J. C. HESSON, R. O. IVINS)

The calculational study to predict the extent of metal-water reaction that would occur during a loss-of-coolant accident in a water-cooled power reactor has continued. The objective of this study is to demonstrate the application of metal-water reaction data to a reactor accident situation. A simple model has been used to calculate the temperature and extent

of reaction throughout the LOFT (Loss of Fluid Test) core assuming that the UO₂-core fuel rods were clad with 25-mil thick zirconium. These calculations have been presented in previous reports (ANL-6925, p. 215 and ANL-7055, p. 192) and in the open litera-

² Design Group, Chemical Engineering Division.

³ This is a facility being developed to conduct engineering tests of the consequences of a loss-of-coolant accident with a pressurized-water power reactor.

ture.⁴ Similar calculations have also been made (ANL-7125, p. 181) for the LOFT reactor assuming that the UO₂-core rods were clad with 15-mil thick stainless steel.

These calculations made use of many simplifying assumptions and ignored heat losses from the core. They did, however, predict the general features of such a loss-of-coolant accident and pointed out several gaps in the knowledge required for a precise analysis. The two major problems uncovered in these analyses were (1) that the availability of steam at the reacting surface would limit the reaction rate, i.e., in order to describe the reaction it would be necessary to calculate the steam-hydrogen mass transfer occurring throughout the core, and (2) that no satisfactory meltdown model exists to describe the collapse of the core and the chemical reaction that occurs during this phase of the accident.

More recently, a program called CHEMLOC (CHEMical reactions following a Loss Of Coolant) has been written for the CDC-3600 computer that takes into account the heat losses from the core and makes use of mass transfer calculations to describe the cladding-steam reaction when limited by the availability of steam at the reacting surface. This program can be used to describe the temperatures of the cladding and UO₂ fuel and the extent of cladding reaction as a function of time until the integrity of the core is lost. The program is described in the following paragraphs.

a. HEAT AND MASS TRANSFER COEFFICIENTS

In order to calculate the heat and mass transfer occurring throughout the core, it is necessary to determine heat and mass transfer coefficients for flow of a fluid through a parallel array of rods. In the previous analyses (ANL-6925, p. 215 and ANL-7055, p. 192), calculations for limited steam conditions were made for flow rates of 0.03 and 0.3 lb/(hr)(rod) [100 and 1000 lb/hr for the LOFT core]. These flow rates were chosen as an order of magnitude estimate for free convection through the core (1000 lb/hr) and a more restrictive flow (100 lb/hr). Steam flow rates of these magnitudes would result in laminar flow. Heat and mass transfer coefficients for laminar flow have been calculated for pipes,⁵ parallel plates,⁵ annuli,⁵ and rods on triangular lattices.⁶

Assuming uniform heat fluxes in laminar flow through

a pipe, duct, or annulus, the Nusselt Number, defined as

$$Nu = \frac{h\ell}{k_g} \quad (1)$$

and the equivalent dimensionless number for mass transfer, defined as

$$Nu_d = \frac{h_d\ell}{D_g} \quad (2)$$

where

h = heat transfer coefficient, cal/(cm²)(sec)(°K),

ℓ = characteristic length, cm,

k_g = thermal conductivity of the gas, cal/(cm)(sec)(°K),

h_d = mass transfer coefficient, cm/sec, and

D_g = diffusivity in the gas, cm²/sec,

become functions of only the geometry as the velocity, temperature, and concentration gradients become fully developed. Thus, the heat and mass transfer coefficients are functions of the fluid conductivity or diffusivity and the geometry of the pipe, annulus, or duct.

An approximate solution for the value of the Nusselt Number for heat or mass transfer applicable to longitudinal laminar flow (fully developed) through an array of cylinders can be obtained from the simple model of an annulus surrounding a cylinder. The inner radius of the annulus is r_o (the radius of the cylinder) whereas the outer radius r' of the annulus is determined so that the flow area associated with each rod is equal to the actual area. With a square array of rods

$$r' = p/\sqrt{\pi} \text{ or } 0.564 p \quad (3)$$

and with a triangular array of rods

$$r' = p/2 \left(\sqrt{\frac{2\sqrt{3}}{\pi}} \right) \text{ or } 0.525p \quad (4)$$

where p is the distance between centers.

Based on this annulus model, the Nusselt Number for heat transfer and for mass transfer can be evaluated. The mathematical techniques have been discussed in several texts^{5, 7-9} and only the result is reported here. In the analysis performed, it was assumed that the heat flux or mass flux per unit length was constant. This assumption is necessary to evaluate the temperature or concentration profiles. The heat and mass transfer coefficients were based on the rod surface temperature and surface concentration and the "cup mixing"

⁴ L. Baker, Jr. and R. O. Ivins, *Nucleonics* **23**(7), 70 (1965).

⁵ Max Jakob, *Heat Transfer*, Vol. 1, John Wiley & Sons, Inc., 1949.

⁶ E. M. Sparrow, A. L. Loeffler, Jr., and H. A. Hubbard, *J. Heat Transfer*, Trans. ASME, Series C, **83**, 415 (November 1961).

⁷ E. R. G. Eckert and R. M. Drake, Jr., *Heat and Mass Transfer*, 2nd Ed., McGraw Hill (1959).

⁸ R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, Inc. (1960).

⁹ C. O. Bennett and J. E. Meyers, *Momentum, Heat and Mass Transfer*, McGraw Hill (1962), Chap. 24.

temperature or bulk temperature and bulk concentration in the gas stream. The Nusselt Number is a function of the ratio of the spacing between the centers of the fuel rods to the rod diameter. However, for values of this ratio from 1.1 to 2.0, the result can be expressed as

$$\text{Nu} = \text{Nu}_d \approx 2.2 \quad (5)$$

where

$$\text{Nu} = \frac{h(r' - r_o)}{k_g}$$

and

$$\text{Nu}_d = \frac{h_d(r' - r_o)}{D_g}.$$

It should be noted that the Nusselt Number in each case is based on the thickness $(r' - r_o)$ of the gas annulus.

This result can be checked numerically with the work of Sparrow et al.⁶ They present a plot of a Nusselt Number for triangularly spaced rods defined as

$$\text{Nu} = \frac{hd}{k_g} \quad (6)$$

where

h = heat transfer coefficient based on bulk gas stream temperature,

d = diameter of rods, and

k_g = thermal conductivity of the gas.

Assuming triangular spacing of 0.375-in. dia. rods on 0.60-in. centers, the heat transfer coefficient from Equation 5 is

$$h = 6.79 k_g [\text{cal}/(\text{cm}^2)(\text{sec})(^\circ\text{K})]. \quad (7)$$

The heat transfer coefficient for such a geometry from the work of Sparrow et al is

$$h = 6.82 k_g [\text{cal}/(\text{cm}^2)(\text{sec})(^\circ\text{K})]. \quad (8)$$

The results for the annulus model developed above agree quite well with Sparrow's results for ratios of center spacing to rod diameter from 1.1 to 2.0. This range of spacings includes those of most current power reactors; for LOFT the ratio is 1.5.

The above results apply where fully developed heat transfer or mass transfer conditions exist. At the entrance and in areas where spacers disturb the velocity, temperature, and concentration profiles, the Nusselt Number and, hence, the coefficients of heat and mass transfer would be larger. However, for laminar flow in pipes, annuli, or ducts where the distances between walls are relatively small and where relatively large thermal conductivities and diffusivities exist in the gas

stream, the equilibrium values are quickly reached. This effect has been discussed in detail elsewhere.^{5, 7, 10}

Eckert⁷ has included graphs suitable for estimating the entrance effects. For the rod diameter and spacing assumed above, calculations based on these graphs indicate that the temperature and flow profiles, and hence steady state values of h and h_d , are developed in a length of about $\frac{3}{4}$ cm (i.e., the entrance effect extends for only $\frac{3}{4}$ cm).

Thus, with distances of one foot or more between spacers, the entrance effects should be negligible in calculating the overall heat and mass transfer. However, those portions of the core where spacers are placed would be expected to react more rapidly under conditions of limited steam flow. Owing to the large chemical energy contribution available, these areas may be subject to early failure. This fact could be important in the consideration of meltdown models and, consequently, the effect of spacers should be considered in any experimental investigation (see Section IV.A.2.).

B. LOSS-OF-COOLANT COMPUTER PROGRAM (CHEMLOC)

The CDC-3600 computer program is based on the solution of five equations that describe the heat and mass transfer and the chemical reactions that occur in an incremental length of fuel rod together with its associated gas flow area. In order to account for spatial effects, a number, n_r , of radial elements is chosen to represent an axial section of a reactor core. In this program, during each time interval, the five equations are simultaneously solved for n_r radial elements in each of a number, n_t , of axial elements, thereby resulting in a solution over the entire core.

The program requires the following information as input:

- 1) Energy distribution in the core as a function of time,
- 2) Steam flow rate into the core as a function of time,
- 3) The initial average fuel and cladding temperatures in the various elements of the core, and
- 4) Physical and chemical (reaction rate constants) properties of core and cladding material as functions of temperature.

The program calculates and prints out the following for the several n_t axial positions in each radial element (n_r elements):

- 1) The average fuel (UO_2) temperature, T_A ,
- 2) The average cladding temperature, T_C ,
- 3) The average gas temperature, T_g ,

¹⁰ H. S. Heaton, W. C. Reynolds, and W. M. Kays, "Heat Transfer with Laminar Flow in Concentric Annuli with Constant Heat Flux," Report No. AHT-5, Stanford University, Stanford, Calif., July 1, 1962.

- 4) The steam concentration in the gas, X , (H_2 concentration is $1 - X$)
- 5) The thickness of cladding reacted, $(r_o - r)$.

Each of the above items is printed out for selected time intervals.

This program incorporates the following features which represent improvements over the previous analysis (ANL-6925, p. 216, ANL-7055, p. 192, and ANL-7125, p. 181).

- 1) Local heat transfer (convection) between the fuel rods and the flowing steam (and hydrogen) is taken into account.
- 2) Mass transfer calculations are used to determine the rate of cladding-steam reaction when the chemical rate law becomes inadequate because of limited steam availability at the reacting surface (see section a, above). This allows calculation of the spatial distribution of hydrogen in the core.
- 3) Radial heat transfer (radiation) and axial heat transfer (conduction) are taken into account. These become important at the edges of the reactor core.
- 4) The heat transfer between the UO_2 core of the fuel rod and the cladding is included in the analysis. This becomes important as the temperatures rise; the large chemical heating effect can rapidly

raise the cladding temperatures, while the UO_2 temperature lags behind. In the previous analysis the UO_2 and cladding were assumed to have a flat temperature profile (i.e., both the UO_2 and cladding were at the same temperature).

- 5) The physical properties of the cladding, fuel, and steam-hydrogen gas stream are included as functions of temperature.

The CHEMLOC program will perform calculations for single rods, small bundles of rods (such as those used in the furnace experiments reported in Section IV.A.1.), large bundles of rods (such as the 19-rod bundles in the proposed laboratory and in-pile experiments reported in Section IV.A.2.), or an entire reactor core. The program has been tested and is currently being used to calculate the results of furnace experiments such as those described in Section IV.A.1. and to improve the type of analysis previously reported for the LOFT core (ANL-6925, p. 216, ANL-7055, p. 192, and ANL-7125, p. 181).

The CHEMLOC program does not take into account the eventual collapse of the core. In order to complete the qualitative analyses of the loss-of-coolant accident, it will be necessary to allow for the loss of integrity of the core materials. This modification will be undertaken after the calculations described above are completed.

4. Studies of Metal-Water Reactions by the Laser Heating Method

(L. LEIBOWITZ, L. W. MISHLER)

Laser-beam heating has proven to be a useful technique for the study of reactions between water and submerged metal particles. The experimental work has been described in detail in previous reports (ANL-6800, p. 327, ANL-6925, p. 198, and ANL-7055, p. 181). A summary of the main findings of the experimental work with aluminum particles is presented herein, together with a recently devised model that satisfactorily describes the reaction process.

a. EXPERIMENTAL RESULTS

Most of the work was carried out with 0.1 by 0.1 by 0.002 cm pieces of aluminum foil. When melted the foils formed spheres of aluminum approximately 0.018 cm in radius. The principal experimental findings utilizing laser-beam heating of these aluminum particles in a water environment are as follows:

- 1) In pure water at room temperature (a pressure of 0.03 atm) the extent of reaction varied between 6 and 11% and was independent of the laser output energy in the range studied—10 to 48 joules (see ANL-6925, p. 199).

- 2) In room temperature water, with one atmosphere of argon overpressure, the extent of reaction was about 1 and 3% at laser energies of 25 and 45 joules, respectively (see ANL-7055, p. 181).

- 3) In water at 100°C (one-atmosphere pressure) and 181°C (ten-atmosphere pressure) no significant reaction was found until a critical laser energy was reached; at this energy and above, complete reaction was observed (see ANL-6925, p. 199 and ANL-7055, p. 182). The threshold energy was the same at both pressures.

- 4) The average time for complete reaction at both 1 and 10 atmospheres of water pressure, as judged from the luminous time on high speed films (see ANL-6925, p. 201), using all the data now available, was about 0.21 sec. Cooling times for unreacted samples were very short, being a few milliseconds.

b. REACTION MODEL

Because of the highly protective nature of oxide films on aluminum, no extensive reaction with water would be expected if the film surrounding the metal remained solid and intact. For aluminum particles introduced

nto propane-oxygen-nitrogen flames,¹¹ for example, an ignition temperature has been identified with the oxide melting point of 2300°K. In the present studies, it would be expected that the aluminum could not be heated above its boiling point by the laser beam. The literature^{12, 13} indicates that in pure water (no inert gas present) at room temperature, the boiling point of aluminum is reached at about 2150°K (the vapor pressure of aluminum being 0.03 atm at that temperature) and the oxide melting point is not attained. (This point was discussed in ANL-6925, p. 203). Reaction in room temperature water thus results from sporadic cracking and rehealing of a solid protective oxide film. The erratic results (6 to 11 % reaction) and the observation of fragile, feathery, fan-shaped oxide formations on residues from reaction in room temperature water support this idea.

When the water temperature is raised to 100°C, it is then possible for the oxide melting point to be reached during the period of heating by the laser pulse. This should occur when a fairly definite amount of energy has been added to the aluminum, and extensive reaction should result if a solid protective oxide film is absent (item 3 above). Once protectiveness has been lost, the rate of reaction seems to be controlled by the rate of diffusion of water through a hydrogen boundary layer surrounding the metal particle. (The water in the cell after reaction was found to be completely free of suspended oxide, thereby indicating that a reaction model could neglect possible vapor phase reaction.)

To test the proposed reaction model, reaction rate and steady state burning temperature calculations were carried out similar to those by Baker and Just (ANL-6548) for the reaction of zirconium and water. The calculations were performed by equating the rate of heat generation with the rate of heat loss and solving the resulting equation.

The rate of heat loss is the sum of losses by convection and radiation and may be written,

$$\text{Heat loss rate} = h(4\pi r^2)(T_s - T_w) + \sigma \varepsilon (4\pi r^2)(T_s^4 - T_w^4) \quad (9)$$

where

- h = heat transfer coefficient,
- r = particle radius,
- T_s = particle surface temperature,
- T_w = water temperature,

¹¹ R. Friedman and A. Maček, *Combustion and Flame* **6**, 9 (1962).

¹² L. Brewer and A. W. Searcy, *J. Am. Chem. Soc.* **73**, 5308 (1951).

¹³ O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry*, 2nd Ed., Pergamon Press, London (1956), p. 322.

- σ = Stefan-Boltzmann constant, and
- ε = emissivity.

The heat transfer coefficient may be written in terms of the Nusselt Number for heat transfer

$$\text{Nu} = h \frac{2r}{k_f} \quad (10)$$

where k_f is the film thermal conductivity. The Nusselt Number for spheres in free convection is given⁸ by

$$\text{Nu} = 2 + 0.6 \left(\frac{(2r)^3 \rho^2 g \Delta T}{\mu^2 T} \right)_f^{1/4} \left(\frac{C_p \mu}{k} \right)_f^{1/3} \quad (11)$$

where

- ρ = density,
- g = gravitational constant,
- $\Delta T = T_s - T_w$,
- μ = viscosity,
- C_p = heat capacity,

and the subscript f indicates that the physical properties are to be evaluated for the H₂-H₂O film surrounding the particle.

The rate of heat generation is simply the product of the rate of diffusion of water through the gas film surrounding the particle and the heat of reaction. This may be written as

$$\text{Heat generation rate} = h_d(4\pi r^2) \frac{\Delta P}{RT_f} Q(T_s) \quad (12)$$

where

- h_d = mass transfer coefficient,
- ΔP = water pressure difference across film,
- $T_f = \frac{1}{2}(T_s + T_w)$, the mean film temperature, and
- $Q(T_s)$ = heat of reaction at T_s .

The coefficient h_d may be related to the Nusselt Number by

$$\text{Nu}_d = h_d \frac{2r}{D} \quad (13)$$

where D = diffusion coefficient, and Nu_d is the Nusselt Number for mass transfer.

The Nusselt Numbers for heat transfer and mass transfer are identical if the diffusion coefficient (D) and the thermal diffusivity ($\alpha = k/\rho C_p$) are equal. Using expressions for the film physical properties given below, the Lewis Number (α/D) is found to be about 1.04, which is sufficiently close to one to allow a single expression for Nu to be used for the evaluation of both h and h_d .

Values for μ , C_p , and k were taken from data tabulated by Svehla¹⁴ and averaged for equimolar mixtures

¹⁴ R. A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA-TR-132 (1961).

of hydrogen and water using the procedure described by Bird, Stewart, and Lightfoot.¹⁵ An empirical equation was found which adequately described these properties in the range of T_f from 1000 to 3000°K. The actual expressions used in the calculations are listed below:

$$k_f = 1.575 \times 10^{-4} + 7.425 \times 10^{-7} T_f \quad (14)$$

$$\mu_f = 1.160 \times 10^{-4} + 2.670 \times 10^{-7} T_f \quad (15)$$

$$C_p = 2.351 T_f^{0.2362} \quad (16)$$

The diffusion coefficient may be expressed by

$$D = 2.493 \times 10^{-5} T_f^{1.75} / P \quad (17)$$

where P is the total pressure. This expression for D was obtained by using the procedure described by Fuller, Schettler, and Giddings.¹⁶

From the expressions for heat generation and for D , it is seen that the rate of heat generation is proportional to $\Delta P/P$. In pure water this ratio is always 1.0 since it is assumed that all the water reaching the particle reacts. In the case where one atmosphere of argon overpressure was employed, however, this ratio is less than one and the reaction rate decreases. The significance of this effect will be discussed in detail later.

In choosing an expression for $Q(T_s)$, it was recognized that the reaction is not adequately described by the equation

The heat generated by this reaction would lead to impossibly high values for the burning temperature. As the temperature of reaction increases, the formation of such species as H, OH, and AlO causes a decrease in the amount of heat liberated. These species must be taken into account in calculating $Q(T_s)$. A computer program using a free energy minimization routine, which had been used to calculate equilibrium adiabatic temperatures and pressures in sodium-air reactions (see Section IV.B.5.), was used to calculate compositions and heats of reaction for the Al-H₂O system. The formation of hydrogen atoms was clearly the most important factor in decreasing the amount of heat generated by reaction at increasing temperature. An equation of the form

$$Q(T_s) = \alpha + \beta T + \gamma T^2 + (\delta/T) \quad (18)$$

was used to fit computed Q values.

Choosing a value for the emissivity of the burning particle was difficult, and calculations were carried out for emissivities ranging from 0.1 to 1.0 for particles in pure water at one atmosphere. The effect of emissivity

on reaction rate proved to be quite small, as would be expected, while the effect of emissivity on temperature increased with increasing particle size. In the particle size range of the laser experiments, however, the effect on temperature was not very great. An emissivity value of 0.3 was used in the subsequent computations.

All the pertinent equations were combined and solved utilizing a CDC-3600 digital computer. The calculated results were then compared with the experimental value for average reaction rate for the 0.018-cm radius particle. The earlier observation of a 0.21-sec reaction time yields an average reaction rate of 1.8×10^{-5} moles H₂O/sec. The calculated average rates at 1 and 10 atmospheres for $r = 0.018$ cm are, respectively, 1.4×10^{-5} and 1.6×10^{-5} moles H₂O/sec. This is in satisfactory agreement with the experimental value.

One additional experimental observation remains to be explained, namely, the observation that, in room temperature water with one atmosphere of argon overpressure, a reaction threshold is not reached and the extent of reaction is small. The explanation for this lies in the dependence of the reaction rate on $\Delta P/P$. In pure water this ratio is always exactly one. With an inert gas present, it is less than one, and the rate of reaction is reduced. In this case, even though the aluminum particle can be heated above the melting point of Al₂O₃ (2300°K), the steady state temperature cannot be maintained above 2300°K, owing to a reduced reaction rate, and the particle is simply quenched. For this case, however, the value of $\Delta P/P$ for water at 25°C, namely 0.03, cannot be used. It has been pointed out¹⁷ that in both the zirconium-water and uranium-water reactions, a value of 0.5 should be used for 25°C water because of the dynamic equilibrium existing at the water-water vapor interface. For the case being discussed here a value for $\Delta P/P$ of about 0.15 or below will suffice to lower the steady state temperature to below 2300°K. The difference between the value of 0.15 and that suggested by Baker of 0.5 probably results from the much higher particle velocities involved in Baker's condenser discharge work.

The proposed model thus seems to account reasonably well for the main features of the reactions observed. It should be emphasized, however, that this model is adequate only for small particles. With massive aluminum samples, additional processes, such as flow of molten metal and widespread rupture of the protective oxide, would be expected to give extensive reaction at temperatures considerably below the 2300°K required for extensive reaction with the small particles that were employed in this work.

¹⁵ R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *op cit*, p. 24.

¹⁶ E. N. Fuller, P. D. Schettler, and J. C. Giddings, *Ind. Eng. Chem.* **58**, 19 (1966).

¹⁷ L. Baker, Jr., *Nucl. Sci. Eng.* **25**, 116 (1966); see also ANL-6548.

5. Photographic Studies of Aluminum-Clad Fuel Plate Samples in TREAT

(R. O. IVINS, L. J. HARRISON,¹⁸ L. LEIBOWITZ)

A series of eighteen photographic experiments was performed to obtain additional information on the in-pile behavior of aluminum-clad fuel materials. (Previous experiments were reported in ANL-6725, p. 212 and ANL-7125, p. 163.) In the present experiments samples of fuel were submerged in room temperature (30°C) water in a photographic capsule (see ANL-7055, p. 191) and exposed to transient bursts of neutrons in the TREAT reactor. High-speed color motion pictures were taken of the samples during the transients. In several cases sample temperatures were measured by means of thermocouples. After the TREAT transients, gas samples were analyzed mass spectrometrically for hydrogen to determine the extent of chemical reaction.

In Figure IV-4 the disassembled in-pile transient equipment used in these experiments is shown. The fuel sample is shown mounted on graphite support pins inside a quartz tube that is partially filled with water. (In later experiments, alumina pins were substituted for the graphite pins and a stainless steel tube with a quartz window was substituted for the quartz tube.) The tube and sample holder assembly are placed inside a stainless steel capsule (inner) to which a quartz window is bolted. Two 1000-watt Sylvania quartz-iodine lamps are also mounted on the front of the inner capsule. The assembly is in turn placed inside a Zircaloy slot liner to which a quartz window is fitted with a gasket seal.

Two types of fuel samples were used in these experiments. The first, Spert 1-D fuel, was a fully enriched 23 w/o uranium-aluminum alloy, 0.020 in. thick and clad with 0.020-in. thick 6061 aluminum. The second, HFIR fuel, was fully enriched 41.45 w/o U_3O_8 -aluminum cermet, 0.030 in. thick and clad with 0.010-in. thick 6061 aluminum. Summaries of the experiments that were conducted with the two types of fuels are presented in Tables IV-1 and IV-2, respectively.

The two fuel types show qualitatively similar behavior in the extents of metal-water reaction. In each case no significant reaction is observed until a threshold energy is reached; from this point on, the extent of reaction increases fairly rapidly with increasing energy input. For the Spert-type fuel, for example, very little reaction is observed until the energy input reaches about 600 cal/g (see also ANL-6725, p. 212). An increase in energy from 620 to 750 cal/g, however, increases the extent of reaction from about 5 to 37%.

Less data are available for HFIR-type fuels, but a similar effect at higher energies is observed. Nuclear energy inputs greater than 700 cal/g were required to

cause more than 2% reaction of the HFIR fuels. It should be noted that the reactor period, which is a measure of the rate of the nuclear energy input to the fuel sample, varied from 0.108 to 0.265 sec in the runs with Spert fuel, and from 0.228 to 0.285 sec in the runs with HFIR fuel. Over this range of reactor periods (0.1 to 0.3 sec), the heat losses from the samples are significantly different for the same energy inputs; the temperature reached by a sample is consequently dependent on the reactor period. Thus, the difference in energy thresholds between the two types of fuel samples is probably a result of differences in reactor periods. Previous experiments in TREAT with HFIR fuel at periods from 0.10 to 0.15 sec (see ANL-7125, p. 163) indicated a threshold energy that is in good agreement with the Spert data.

It was noted that after the first transients in which the alumina support pins were used (MWT-8, -9, and -10), the resolidified sample adhered to the alumina support pins. Since the samples were relatively immobile even though melted, a technique was developed to obtain temperature data during the transient using 0.010-in. thermocouple wire. As may be seen in Tables IV-1 and IV-2, the thermocouples in experiments MWT-13 (Spert) and MWT-15 (HFIR) indicated temperatures slightly greater than 1400°C. Melting of the chromel-alumel wires used as thermocouples was observed in these experiments, and consequently, the

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FIG. IV-4. In-Pile Assembly for Photographic Study of Metal-Water Experiments in TREAT.

¹⁸ ANL Idaho Division.

TABLE IV-1. SUMMARY OF SPERT-TYPE FUEL EXPERIMENTS

Exp. No.	Transient Number	Integrated Power (Mw-sec)	Period (sec)	Fission Energy Input (cal/g)	Aluminum Reacted (%)	Comment
MWT-1	848	31	0.265	84	0	Calibration run
MWT-2	849	65	0.261	197	0	Calibration run
MWT-14	947	70	0.285	212	0	Boiling of water; no sample reaction
MWT-3	850	147	0.139	445	0	Corner melted
MWT-8	929	157	0.162	485	<1	Melted into globule
MWT-4	851	159	0.139	481	0	Melted into globule
MWT-7-1	897	69	0.265	209	0	Boiling of water; no sample reaction
MWT-7-2	898	163	0.140	493	0.25	Two-thirds of the sample melted
MWT-13	939	176	0.115	532	0.8	Melted into globule ^a
MWT-9	930	177	0.113	536	1.2	Melted and formed hull-shaped mass
MWT-10	931	205	0.108	621	5.3	Al ₂ O ₃ clouded water
MWT-11	932	220	0.108	666	13.6	Fragmented
MWT-12	938	230	0.108	696	10.6	Fragmented
MWT-18	956	248	0.109	751	37	1920°C measured, sample fragmented

^a Thermocouple failed after indicating 1400°C.

TABLE IV-2. SUMMARY OF HFIR-TYPE FUEL EXPERIMENTS

Exp. No.	Transient Number	Integrated Power (Mw-sec)	Period (sec)	Fission Energy Input (cal/g)	Aluminum Reacted (%)	Comment
MWT-5	862	21	0.270	170	0	Calibration
MWT-6	863	65	0.265	530	0.2	Cladding partially melted, blow hole
MWT-15	948	81.5	0.285	662	1.8	Sample melted, ^a UO ₂ layer visible
MWT-16	952	85.5	0.280	694	1.7	Cladding melted, corner of fuel plate melted
MWT-17	955	99	0.280	805	12	2060-2230°C, fragmented, UO ₂ layer visible

^a Thermocouple failed after indicating 1400°C.

measured temperature is not necessarily the maximum sample temperature.

Figures IV-5 and IV-6 show the temperature data obtained using W-5 % Re/W-26 % Re thermocouples in experiments MWT-17 (HFIR) and MWT-18 (Spert). (In MWT-17, intermittent contact was apparently being made between the sample and the thermocouple junction, as indicated by the cross-hatched area in Figure IV-5.) In both of these experiments sample breakup coincided with a temperature approximately equal to the boiling point of aluminum (2270°C), while general vapor phase burning was observed to occur initially at temperatures between 1700 and 1800°C. This observation is in good agreement with previously described (ANL-6648, p. 196) laboratory results obtained with aluminum. In the laboratory study, ~8-mm dia. spheres that were heated and levitated in an induction coil ignited at a temperature of 1750°C in flowing steam.

The general sequence of events as observed in the motion pictures taken during the transients is outlined below:

a) Power rises¹⁹

¹⁹ Seen on film as counting marks.

b) Water boils

c) Melting occurs, Spert fuel melts to globule, HFIR cladding slumps and develops holes

d) Glowing observed, H₂ bubbles form

e) HFIR samples fuse to globules

f) Brightness increases and a vapor phase reaction occurs as indicated by oxide smoke clouding water

g) Sample fragments

h) Sample reacts until quenched

This sequence of events is illustrated for a sample of Spert fuel in Figure IV-7 in which a number of selected frames of the high speed film are shown.

It is interesting to note that fragmentation occurs only after the reaction begins to take place in the vapor phase. The fragmentation apparently results from the motion of the water column. The water is initially forced upward by the formation of vapor bubbles; the return of the water collapses the bubbles and causes the samples to fragment. A similar phenomenon was observed when metal particles at the bottom of a water column were heated with a laser beam (see ANL-690 p. 253). In that work, it was observed that the particles were forced to the bottom of the vessel quite violently by the motion of the water column, often with sample

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FIG. IV-5. Sample Temperature and Reactor Power Record during TREAT Transient MWT-17.

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FIG. IV-6. Sample Temperature and Reactor Power Record during TREAT Transient MWT-18.

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Fig. IV-7. Selected Frames of High Speed Motion Picture of Spert Fuel Undergoing a Nuclear Transient in TREAT.

break-up resulting. The observation that fragmentation occurs only after the vapor phase reaction begins is important. Prior to these photographic experiments, fragmentation was thought to occur before ignition (vapor phase reaction) in the TREAT experiments.

As a result of the photographic studies (plus other earlier nonphotographic experiments), the following qualitative description of the aluminum-water reaction in the TREAT experiments now seems evident.

- 1) Below temperatures of 1750°C , the reaction of aluminum is characterized by the formation of a protective oxide and the evolution of hydrogen bubbles (as seen in the films). The samples rapidly quench after the nuclear burst and only limited reaction occurs. This must be true in both subcooled (30°C) and heated water, although it has been observed photographically only in the former.
- 2) At 1750°C , a vapor phase reaction occurs and an ignition results in which self-heating raises the sample temperature several hundred degrees (to $>2000^{\circ}\text{C}$). This is believed to occur both in subcooled and in heated water. The extent of reaction depends on the length of time that the burning persists.
- 3) In subcooled water (30°C), violence due to agitation of the water causes fragmentation of the sample. Some of the particles are quenched by striking cooler portions of the container while others continue to burn until small enough (~ 2 to 3 mm) to be quenched (see ANL-6800, p. 338). Thus the

extent of reaction depends on the violence and the manner of quenching of individual particles.

- 4) In heated water, no fragmentations have been noted even though ignition and very extensive reactions do occur at the higher energies. The violence in the heated water must be less; however, motion pictures have not been taken under these conditions.

In applying the TREAT results to reactor calculations, care must be taken to choose the correct correlating parameter. In a previous report (ANL-6725, p. 218), calculations of the extent of reaction occurring in the destructive test of the Spert I reactor and in the accidental excursion of the SL-1 reactor were described using the TREAT results. In these calculations, the temperatures reached in the various sections of the reactor cores were estimated assuming no chemical heating. It was then necessary to estimate the sample temperature of the TREAT experiments due to *fission heating alone*; actual temperatures reached in the reactor are a result of both chemical and fission heating. The relatively long period of the transients in the TREAT experiments causes significant heat losses and temperatures cannot be calculated by assuming adiabatic conditions. At low energies where little or no chemical reaction occurs, the examination of sample residues for evidence of incipient sample melting established the energy input that was equivalent to a temperature of 660°C (aluminum m.p.). In the calculations described in ANL-6725, a temperature range of 1200 to

1400°C was assigned to the energy at which ignition occurred. A correlating temperature of 1400°C for ignition still seems appropriate; this is based on more recent observations that samples at energies slightly below that required for ignition gave measured temperatures only a little higher than 1400°C (possibly as high as 1500°C to 1600°C). However, after allowing for chemical heating, 1400°C seems a reasonably conservative estimate of the proper correlating temperature for the ignition threshold.

One final observation concerning this study needs to be made. A thermite reaction between aluminum and U_3O_8 would be expected to occur in the experiments with HFIR fuel samples. In previous laboratory studies with 40 w/o U_3O_8 -aluminum compacts (see ANL-6900,

p. 303), a thermite reaction was observed for samples heated to 1000°C. Self-heating rates of about 100 to 200°C/sec were measured in those experiments. During the TREAT transients, the HFIR fuel plates (41.45 w/o U_3O_8) were subjected to heating rates which were at least an order of magnitude greater than the rates attributable to the thermite reaction. Thus, it is not surprising that no evidence of the thermite reaction was observable on the temperature records of the experiments. However, in experiments MWT-15 and MWT-17, a layer of brown UO_2 (identified by X-ray diffraction) was visible on the edge of the samples, indicating that the thermite reaction did occur with these samples.

6. Studies in TREAT of Zircaloy-2-Clad, UO_2 -Core Simulated Fuel Elements²⁰

(R. C. LIIMATAINEN, F. J. TESTA)

Experiments were continued in TREAT to investigate the safety problems associated with the behavior of metal-clad, UO_2 -core simulated fuel elements. The purpose of the current tests is to obtain information on the chemical and physical changes which take place upon meltdown of fuels in a nuclear reactor undergoing a power excursion. Specific emphasis is placed on determining the extent of metal-water reaction, the peak pressure produced, and the final particle size distribution of the fragmented fuel samples; these parameters are then correlated as a function of the energy of the reactor pulse.

The basic experimental technique consists of loading an autoclave with the fuel samples submerged in water and subjecting the autoclave to a burst of neutrons in TREAT. The fission heat generated in the enriched UO_2 core of the fuel samples by the neutron burst causes meltdown of the test rods. After the transient, the hydrogen evolved is measured by means of a mass spectrometer, and from this the amount of metal-water reaction is computed. Also, sieve-screen analyses are made on the residue from the fragmented fuel to determine the particle size distribution, from which the mean size is calculated.

Previously, as part of this program, data were obtained using single UO_2 -core pins clad with either Zircaloy-2 or type 304 stainless steel (see ANL-6900, p. 254). Also, transient experiments in a scale-up autoclave were conducted with clusters of 9 rods (see ANL-6925, p. 209 and ANL-7125, p. 170); these experiments are designed to simulate the meltdown of a subassembly, or portion of a reactor core, during a power

excursion. Recent experiments have also utilized both single pins and clusters of rods of UO_2 -core fuel clad with Zircaloy-2.

a. EXPERIMENTS WITH SINGLE FUEL PINS

Three transients were conducted in TREAT with single pins to obtain additional data at high fission energy inputs on the meltdown behavior in water of Zircaloy-2-clad, UO_2 -core fuel. Fuel elements of this type are currently being used in thermal power reactors. Previous data on the same type of single fuel pins were reported in ANL-6900, p. 265. The additional transients reported herein were run to extend the data and establish more firmly the correlation of nuclear energy input and extent of metal-water ($\text{Zr-H}_2\text{O}$) reaction. Especially needed was more information in the region of high energy input that corresponds to partial vaporization of the UO_2 .

Table IV-3 gives a summary of the results from this series. Each of the fuel pins underwent complete destruction with extensive metal-water reaction and formation of fine particles.

The oscillograph records of the three experiments are shown in Figures IV-8, IV-9, and IV-10. The records are particularly significant in that each one documents a very rapid, yet nonexplosive, rate of pressure rise inside of the autoclave. The pressure-time curve shows a characteristic, rather sharp rise of a few thousand psi per second to the peak value. This is followed by a region of declining pressure with time. The rise is caused by the generation of steam and hydrogen and the fall is caused by condensation of the steam and general cooling of the gas phase inside of the autoclave. The final equilibrium pressure is then the sum

²⁰ We gratefully acknowledge the cooperation of James Bolland and the TREAT personnel of the ANL Idaho Division.

TABLE IV-3. SUMMARY OF RECENT ZIRCALOY-2-CLAD, UO₂-CORE SINGLE PIN^a MELTDOWN EXPERIMENTS IN TREAT

	CEN-TREAT Transient Number		
	214	215	216
<i>Transient</i>			
Integrated power, Mw-sec	416	663	749
Peak power, Mw	1415	2965	4050
Period, msec	73	49	42
Fission energy input, cal/g UO ₂	375	595	675
<i>Results</i>			
Zr-H ₂ O reaction, %	13	21	68
Peak pressure, psig	430	238	567
Maximum rate of pressure rise, psi/sec	3600	1700	5500
Mean particle size (d_{sv}), ^b mils	24	19	13
Fuel appearance after transient	Complete fragmentation, particles and fines	Complete fragmentation, particles and fines	One large globule, particles and many fines

^a One sintered pellet of UO₂, 11.2% enriched, 0.5 in. long by 0.375 in. OD.

^b $d_{sv} = \frac{1}{\sum \frac{W_i}{d_i}}$, where W_i = fraction of particles by weight with diameter d_i .

of the partial pressures of the hydrogen evolved, the water vapor, and helium. Analysis of the pressure-time records is being continued for all of the meltdown experiments performed thus far in this TREAT program. Tentatively, it appears that transients having a nuclear energy input less than 400 cal/g UO₂ always have a relatively modest pressure rise rate of the order of 100 psi/sec. For meltdowns in water from power excursions of 500 cal/g UO₂ or more, there is a pressure pulse that has a rise rate of a few thousand psi/sec, increasing progressively with energy input. Between 400 and 500 cal/g UO₂, there seems to be a transition region where either behavior can occur.

b. EXPERIMENTS WITH VIBRA-PACKED UO₂-CORE FUEL

Two transients with Zircaloy-2-clad, vibrationally compacted and pneumatically impacted UO₂-core fuel²¹ have recently been completed. The primary purpose of these two experiments was to compare the meltdown behavior in water of simulated fuel elements with and without a high internal gas pressure. These experiments also permitted a comparison of the behavior of the vibra-packed UO₂ fuel with that of sintered UO₂ fuel. The experiments were conducted with 4-rod clusters in the scale-up autoclaves. One cluster of rods was fabricated with a 1500 psia helium internal gas pressure in each rod to simulate fission product gases. The helium in the fuel rods of the other cluster was at 15 psia.

Vibrational compaction and pneumatic-impaction (a closed-die, hot-forging technique) produces oxide fuel

particles of nearly theoretical density for use in the fabrication of packed-particle fuel elements. The slightly hyperstoichiometric (O:U ratio, 2.02) fuel material prepared by this process has an average sorbed gas content of 0.07 cc/g. Each rod contained approximately 110 g of UO₂ fuel (15% enriched) with a bulk density of 81% of theoretical density. The particle size distribution of the as-loaded UO₂ fuel, which had a calculated mean particle size (d_{sv})²² of 6 mils, is as follows:

Tyler mesh size	Average diameter of particles in size group (mils)	% by weight
-6 +10	100	55.0
-20 +35	25	12.5
-35 +65	12	12.5
-200	1.5	20.0

Figure IV-11 shows a fuel rod cluster prior to a transient and the meltdown residues following the two experiments. The data for the two runs, presented in Table IV-4, show that, in general, the pressurized and unpressurized fuel rods behaved similarly. The extents of metal-water reaction and the average particle sizes of the fragmented fuels were nearly identical. The particle size-frequency distributions of the fragmented fuels were also nearly the same.

The oscillograph records of the two runs (shown in Figure IV-12) indicated that the fuel rods with the

$$^{22} d_{sv} = \frac{1}{\sum \frac{W_i}{d_i}}, \text{ where } W_i = \text{fraction of particles by weight with diameter, } d_i.$$

²¹ The fuel elements were prepared by M. Freshley of Hanford-Battelle Laboratory.

Fuel pin after transient

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FIG. IV-8. TREAT Transient CEN-214, Zircaloy-2-Clad, UO_2 -Core Fuel Pin.

Oscillograph record

Fuel pin after transient

308-202 T-1

FIG. IV-9. TREAT Transient CEN-215, Zircaloy-2-Clad, UO_2 -Core Fuel Pin.

simulated fission product gases (1500 psia internal pressure) failed initially at a lower temperature than the ones with an internal gas pressure of 15 psia. A thermocouple attached to the Zircaloy-2 cladding of one of the fuel rods in this latter run (CEN 218S) indi-

cated a temperature of 1750°C , after which its behavior became erratic; this is close to the melting point of th Zircaloy-2, and no doubt corresponds to it within the accuracy of the temperature measurement. If it is assumed that the initiation of the erratic behavior of the

Oscillograph record

Fuel pin after transient

308-201 T-1

FIG. IV-10. TREAT Transient CEN-216, Zircaloy-2-Clad, UO_2 -Core Fuel Pin.

Before

CEN-218S after

CEN-219S after

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FIG. IV-11. Zircaloy-2-Clad, Vibra-Packed UO_2 -Core Fuel Clusters Before and After Transient Meltdown in Water.

thermocouple corresponded to the time of fuel rod failure, at this point approximately 85 % of the total energy of the transient had been deposited in the fuel cluster (i.e., 85 % of 467 cal/g UO_2 or ~ 400 cal/g UO_2). The cladding temperature of the pressurized fuel cluster (run CEN 219S) was only 550°C when a similar erratic behavior of the thermocouple attached to a fuel rod occurred. At this time during the reactor transient, only 30 % of the total nuclear energy (471 cal/g UO_2) had been released. This is equivalent to a fission energy input of 142 cal/g UO_2 .

The pressure in the autoclave in the run with the pressurized fuel cluster (run CEN 219S) began to rise earlier in relation to the reactor power burst than that in the autoclave with the unpressurized fuel (CEN 218S). However, the maximum rise rate and the maximum pressure of the former was lower (see Table IV-4).

From these results, the fuel failures in the two fuel clusters with vibra-packed UO_2 appear to have occurred by two different mechanisms even though the overall results were very similar. The two mechanisms are postulated to be as follows:

Type of UO ₂ Fuel Rod	Relative Time of Failure During Power Burst	Mechanism of Fuel Rod Failure
Unpressurized (15 psia)	Toward end of transient	Melting of Zircaloy-2 cladding, UO ₂ also molten
Pressurized (1500 psia), simulated fission product gas	Initial failure early in transient, continuing as power input increased	Internal gas pressure exceeds ultimate strength of solid Zircaloy-2 cladding; both UO ₂ and Zircaloy-2 still solid when fuel fragmentation commences

Assuming adiabatic heating, the UO₂ core of the fuel rods with the 1500 psia internal pressure would have reached ~2000°C at the indicated time of failure. If the helium inside the fuel rods were also at the same temperature as the vibra-packed UO₂, the gas pressure would have risen from 1500 psia initially, to 11,350 psia at 2000°C. From the relationship which is applicable to a cylindrical jacket,

$$\sigma_t = \frac{Pr}{t}, \quad (19)$$

where

P = internal pressure = 11,350 psi,

r = internal radius of cylinder (cladding) = 0.25 in.,

t = thickness of cladding = 0.030 in.

The calculated stress is $\sigma_t \cong 95,000$ psi. At 500°C, the ultimate or tensile strength of Zircaloy-2 is 32,000 psi. Since the calculated stress of 95,000 psi exceeds the ultimate stress of 32,000 psi, it is evident that the indicated time of initial fuel failure for run CEN 219S is not inconsistent with the postulated failure mechanism.

The extent of reaction was similar in the two experiments (see Table IV-4), suggesting that the ultimate dispersion mechanisms were similar. Although failure of the pressurized cluster of rods probably began at a lower temperature, the final dispersion mechanism probably required melting of the UO₂ and resulted in similar cladding temperatures being reached in both experiments.

The correlations which are given in Figures IV-13 and IV-14 illustrate the similarities and differences between the behavior of the vibra-packed UO₂-core fuel rods and the sintered (pellet) UO₂-core fuel rods previously tested (ANL-7125, p. 170). In particular, the extent of chemical reaction (i.e., Zr-H₂O reaction) seems to be independent of the type of UO₂ in the core.

TABLE IV-4. SUMMARY OF TREAT EXPERIMENTS WITH ZIRCALOY-2-CLAD, VIBRA-PACKED UO₂-CORE FUEL ROD CLUSTERS SUBMERGED IN WATER.
4 rods^a per cluster

	CEN-TREAT Transient Number	
	218S	219S
<i>Transient</i>		
Internal fuel rod pressure, He psia	15	1500
Integrated power, Mw-sec	407	411
Peak power, Mw	1280	1275
Period, msec	74	75
Fission energy input, cal/g UO ₂	467	471
<i>Results</i>		
Zr-H ₂ O reaction, ^b %	45	38
Peak autoclave pressure, psig	800	700
Max. pressure rise rate, psi/sec	4000	3000
Total (chemical and nuclear) energy released, cal/g H ₂ O	416	385
% Chemical energy release ^c	51	46
Mean particle size after transient (d_{sv}), ^d mils	36	30
Fuel appearance after transient	Complete fragmentation, particles and fines	Complete fragmentation, particles and fines

^a Each rod was 9.5 in. long by 0.566 in. OD and contained 110 g UO₂ (15% enriched) packed to 80% of theoretical density.

^b Calculated on the assumption that all of the evolved hydrogen (measured by mass spectrographic analysis) resulted from the reaction $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$.

^c % Chemical Energy Release = $\frac{\text{chemical energy}}{\text{total (chemical + nuclear) energy release}} \times 100$.

^d $d_{sv} = \frac{1}{\sum \frac{W_i}{d_i^3}}$, where W_i = fraction of particles by weight with diameter, d_i .

CEN-218S
15 psia He internal pressure

CEN-219S
1500 psia He internal pressure

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FIG. IV-12. Oscillograph Records of TREAT Experiments with Vibrationally Compacted UO_2 Fuel Rods. (Zircaloy-2 cladding.)

As shown in Figure IV-13, the observed metal-water reaction with the vibra-packed UO_2 -core fuel rods agrees very well with data previously obtained with rods and pins having sintered UO_2 pellets in the core.

A distinct contrast in physical behavior is evident in Figure IV-14.²³ The peak pressures generated in the experiments with the vibra-packed fuel are well above

²³ The points designated in Figure IV-14 as "Zr" and "SS" represent Zircaloy-clad and stainless steel-clad, sintered UO_2 -core fuel, respectively; the points designated as "U" represent unclad uranium metal fuel.

the pressures generated in those with the sintered UO_2 fuel clusters. This difference is believed to be a result of differences in particle size of the residue. The vibra-packed fuel breaks up into much finer particles, and the larger surface area allows more rapid heat transfer to the water. This, in turn, would tend to give rise to a more energetic steam pressure pulse. Specifically, as noted in Table IV-5, the mean particle sizes²⁴ resulting

²⁴ The Sauter mean particle diameter, d_{sv} , is a linear function of the particle surface area. It is defined as

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FIG. IV-13. Results of Meltdown Experiments in TREAT on Zircaloy-2-Clad, UO_2 -Core, Simulated Fuel Elements Submerged in Water. (Water at 30°C and 20 psia, except as noted.)

from power burst of equal magnitude for the fuel clusters submerged in water are about 30 mils for vibra-packed UO_2 fuel rods and approximately 100 mils for the sintered UO_2 fuel rods. Thus, about three times as much surface area is produced in the case of the vibra-packed UO_2 . The peak pressures in the experiments with vibra-packed UO_2 averaged about 750 psig, whereas in the earlier experiments with sintered UO_2 , the peak pressures were about 250 psig. Thus the ratio of the peak pressures and the ratio of the surface areas are the same, namely, 3. It seems reasonable to conclude, at least in a semi-quantitative way, that the surface area had an important bearing on the peak pressures observed.

Another significant observation concerns the initial rate of pressure rise. The data in Table IV-5 and Figure IV-14 indicate that although a direct proportionality appears to exist between the magnitude of the pressure rise and the surface area of the residue, the rate of

$$d_{av} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} = \frac{1}{\sum \frac{W_i}{d_i}},$$

where n_i = number of particles and W_i = fraction of particles by weight with diameter, d_i .

pressure rise does not show such a linear dependence on the surface area. For example, the meltdown of vibra-packed UO_2 caused an initial pressure rise rate of 4000 psi/sec (as determined from the slope of the pressure-time record on the oscillograph of the transient), whereas in the case of the sintered UO_2 , the rate of

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FIG. IV-14. Peak Pressure Rise in TREAT Metal-Water Scale-up Experiments as a Function of the Total Energy (Chemical + Nuclear) Released per Gram of Water in the Autoclave.

TABLE IV-5. UO_2 FUEL CLUSTER POWER EXCURSION EXPERIMENTS IN TREAT: A COMPARISON OF THE OBSERVED MAXIMUM PRESSURE RISE RATES AND MEAN PARTICLE SIZES FROM MELTDOWNS IN WATER^a

	Type of UO_2 in Core of Fuel Rod			
	Sintered		Vibra-packed	
Transient number	208S	209S	218S	219S
Cladding	SS	Zr	Zr	Zr
Energy, cal/g UO_2	475	485	467	471
Max. pressure rise rate, psi/sec	17	40	4000	3000
Mean particle size of residue (d_{ss}), mils	95	132	36	30

^a Comparison is made at similar energy inputs for each run.

pressure rise was relatively modest, 40 psi/sec. Thus, the ratio of the pressure rise rates is approximately 100 for the same energy inputs to the UO_2 .

It also should be mentioned that the results with vibra-packed UO_2 might be strictly applicable only to cold, clean fuel. It is conceivable that once vibra-packed UO_2 has been in an operating reactor at high temperature for an extended period of time, the fuel might behave more like sintered UO_2 .

It is of interest to compare the correlation shown in Figure IV-13, which includes all in-pile experiments in TREAT with Zircaloy-2-clad, UO_2 -core fuel samples, with data from the out-of-pile condenser discharge experiments. These experiments were reported in ANL-6333, p. 218 and in ANL-6548.

In the condenser discharge experiments, 30- and 60-mil zirconium wires submerged in water were rapidly

TABLE IV-6. RESULTS FROM IN-PILE (TREAT) MELTDOWN EXPERIMENT CEN 217S: UO_2 -CORE, ZIRCALOY-2-CLAD FUEL CLUSTER SUBJECTED TO FLAT-TOP TRANSIENT

<i>Fuel Cluster</i>	
No. of fuel rods ^a	3
Cladding ^b	Zircaloy-2
Weight, g	336 ^c
<i>Transient</i>	
Type of incident simulated ^d	Loss-of-coolant
Fission energy input, cal/g UO_2	560
Time of heating, sec	12
Peak adiabatic UO_2 temperature, °C	3300 (Vapor region)
<i>Results</i>	
Zr- H_2O reaction, %	40
Peak pressure rise, psi	87
Total (chemical and nuclear) energy released, cal/g H_2O	260
Chemical energy release, % of total energy	26
Average particle size of residue (d_{av}), ^e mils	
Residue remaining above water	240
Residue in water	50
Total residue	91
Appearance of Fuel after Meltdown	Complete destruction; molten UO_2 ran out, leaving sections of hollow cylinders of the Zircaloy cladding.

^a Ten pellets of UO_2 (10% enriched with ^{235}U) per rod. Overall rod dimensions were 0.42-in. dia. by 55½ in. long.

^b 25-mil thick cladding; 3-mil gap between core and cladding; helium bonded.

^c 254 g of UO_2 and 82 g of Zircaloy-2.

^d The fuel rods were suspended above ambient temperature water.

$$^e d_{av} = \frac{1}{\sum \frac{W_i}{d_i}}, \text{ where } W_i = \text{fraction of particles by weight}$$

with diameter, d_i .

heated with an electrical discharge from a bank of condensers; with sufficient electrical energy the wires were fragmented into particles. The subsequent reaction of the wire was found to be a function of initial metal temperature, particle size, and water temperature. In the TREAT experiments it is impossible to measure the cladding temperatures accurately after melting occurs. It is also difficult to obtain meaningful particle size data (i.e., surface area available for reaction) from the TREAT experiments.

A qualitative comparison can be made, however, between the results of the two experimental techniques. In Figure IV-13, the extent of reaction when the cladding reaches its melting temperature can be seen to be about 10%; this corresponds to the threshold energy of fuel failure (~ 280 cal/g UO_2). As the energy input increases, more extensive reaction occurs and it is reasonable to assume that the initial cladding temperature increases to about 3300°C at the highest energy inputs. The data in Figure IV-13 can be compared with the results of the condenser discharge experiments (ANL-6548, p. 49) in room temperature water. (All but two of the TREAT experiments shown in Figure IV-13 were conducted in water initially at 30°C.) In the condenser discharge experiments, at an initial metal temperature corresponding to the melting point of zirconium (1852°C), an average of 10% reaction was found. As the initial metal temperature was increased, the extent of reaction also increased and was about 70% at temperatures near 3300°C. These results agree quite well with those shown in Figure IV-13.

c. LOSS-OF-COOLANT SIMULATION EXPERIMENT (FLAT-TOP TRANSIENT)

An experiment has been performed in TREAT in which three Zircaloy-2-clad, UO_2 -core fuel rods were melted down while suspended above a pool of water. The purpose of this experiment was to simulate certain aspects of a loss-of-coolant accident in which a break in a primary system water pipe of a nuclear power reactor would result in contact of the fuel elements with steam at high temperature. (A calculational study estimating the extent of the subsequent cladding-water reaction has been previously reported in ANL-6925, p. 215; ANL-7055, p. 192, and in the open literature.⁴)

The experimental assembly used was that previously described for scale-up experiments (see ANL-6925, p. 209). However, the experiment differed from the previous scale-up experiments with UO_2 -core fuel in which the transients simulated power excursion incidents (see ANL-7055, p. 190 and ANL-7125, p. 170), as follows:

(1) The fuel cluster consisted of 3 rods (0.42-in.

Upper portion (out of water)

Lower portion (within water)

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FIG. IV-15. Residue from Zircaloy-Clad UO₂-Core Fuel Rods after TREAT Transient CEN-217S Simulating a Loss-of-Coolant Incident

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FIG. IV-16. Oscillograph Record of TREAT Transient CEN-217S.

dia. by 5% in. long) rather than 9 rods as previously tested.

- (2) The fuel rods were located above a pool of water rather than submerged in it.
- (3) The meltdown was achieved during a "flat-top" transient rather than a pulse.²⁵

The results of this experiment are summarized in Table IV-6. In this meltdown, 38 w/o of the fuel cluster dropped into the water, although the larger particles tended to be retained above the water by the fuel rod support structure. (Figure IV-15 illustrates the smaller average particle size of the residue collected in the water compared with that of the residue remaining above the water.) The extent of cladding-water reaction was determined to be 40% by measuring the total amount of hydrogen released; however, it was not apparent whether the cladding that had dropped into the water was more extensively reacted than the cladding that had remained on the support structure. All of the hydrogen produced was assumed

²⁵ In the "flat-top" transient, fission heating remained reasonably constant over a period of about 12 sec. In a pulsed transient, the time scale for heating is about 1 sec, with a Gaussian-shaped power-time heating curve. It should be emphasized, however, that even though the time scale for the flat-top transient was an order of magnitude longer than for the earlier TREAT pulsed transients, 12 sec is still quite short compared to anticipated times for an actual loss-of-coolant event with decay heating.

to be formed by reaction of the Zircaloy cladding. The reaction of the UO_2 core with water would be expected to become significant only after the cladding was completely oxidized, since the presence of excess hydrogen greatly suppresses the UO_2 -water reaction (see ANL-7125, p. 159). The chemical energy contributed by the reaction corresponded to 26% of the total energy (i.e., the contribution of the nuclear energy of the transient was 74%).

The oscillograph records of the temperature and pressure measurements from the experiment are shown in Figure IV-16. (It will be noted that the peak pressure rise is in agreement with the correlation shown in Figure IV-14.) The sequence of events deduced from Figure IV-16 and from the appearance of the residue may be summarized as follows:

Time (sec)	Energy Input (cal/g UO_2)	Event
0	0	Initiation of fission heating.
7	360	Thermocouple on the Zircaloy cladding records 2430°C and fails, indicating that fuel slumping has begun.
~8.2	480	Pressure rises rapidly owing to the formation of steam and/or evolution of hydrogen, indicating that fragments of fuel are probably entering the water.
~9.3	500	Thermocouple in the water records rapid temperature rise, indicating that the fuel has made contact with the thermocouple (temperature recorded in excess of 1000°C).
12	560	End of heating; pressure rises only very slowly, indicating end of the reaction.

One of the most interesting and significant points in connection with this experiment was the final appearance of the meltdown residue. This was the first time that portions of the cladding were found still in their original cylindrical form, but with the UO_2 core not present. Evidently, the UO_2 had melted and flowed out of the cladding. However, the melted cladding material did not separate from the unmelted portion. Large globules attached to the unmelted cladding can be seen in Figure IV-15. This observation is important in developing the meltdown model for the loss-of-coolant accident. Since the molten cladding material does not leave the reactor core, it can react with available steam at a very rapid rate.

Since the energy developed in this experiment (560 cal/g UO_2) was high enough to vaporize the UO_2 adiabatically and the time scale (12 sec) was relatively short, the experiment was not an exact simulation of a loss-of-coolant accident. Therefore, the extent of reaction is not directly comparable to what

might be expected in such a situation. Nevertheless, the residue shown in Figure IV-15 gives some indica-

tion of the meltdown model that must be considered in the analysis of this type of incident.

B. FAST REACTOR SAFETY STUDIES

1. Fuel-Coolant and Cladding-Coolant Interaction Studies (F. J. TESTA, J. PAVLIK, R. O. IVINS)

Experiments have been conducted to determine the nature and magnitude of safety problems that might arise in the event that abnormally hot fuel and cladding materials come in contact with the coolant (usually sodium) in a fast reactor. In a survey study, small heated samples of fuel or cladding materials were dropped into heated sodium (see ANL-6925, p. 226, ANL-7055, p. 199, and ANL-7125, p. 187). No chemical interaction of any of the materials was observed; however, extensive fragmentation of molten cladding metals did occur. An hypothesis was developed (see ANL-7125, p. 191) to explain the mechanism of fragmentation.

More recently, this investigation has been concerned with determining the mean particle sizes of the various metal residues, particularly those from type 304 stainless steel samples, resulting from the fragmentation process. The metal residues were first sieved, using sieve screen sizes from 1 to 500 mils, and then the several fractions were weighed. From the weight-size distribution of each "drop", the mean size was calculated by the relationship

$$d_{sv} = \frac{1}{\sum \frac{w_i}{d_i}} \quad (20)$$

where d_{sv} is the Sauter mean diameter and w_i is the fraction of particles by weight which have the diameter, d_i .

In Figure IV-17, the mean particle sizes of the residues of type 304 stainless steel samples dropped into 250°C sodium are shown. The temperatures of the samples ranged from 1425 to 2400°C when they were dropped. It can be seen from Figure IV-17 that total fragmentation occurs when the drop temperature exceeds 1600°C. At drop temperatures greater than 2000°C, the mean particle size of the residues is seen to approach about 10 mils.

Samples of type 304 stainless steel were also dropped into liquid sodium which had been heated to temperatures as high as 820°C. The mean particle sizes determined for the residues from these experiments were as follows:

Sodium Temperature (°C)	Sample Drop Temperature (°C)	Mean Particle Size, d_{sv} (mils)
250	2150-2400	~10
720	2200	6
800	2200	4
820	2300	3

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FIG. IV-17. Particle Size Distribution of Type 304 Stainless Steel Samples Dropped into 250°C Sodium.

Thus, the effect of the higher sodium temperature was a more thorough fragmentation of the residue.

Mean particles size determinations were also carried out for type 304 stainless steel residues from drops into molten lithium and potassium. These measurements indicated that fragmentation in lithium was slightly less extensive than in sodium under similar

conditions, whereas fragmentation in potassium was substantially the same as in sodium.

These data provide a quantitative measure of the degree of fragmentation that can be correlated with the previously delineated mechanism of fragmentation.

2. Transient Heat Transfer Studies: Measurement of Heat Flux from a Heated Metal Sphere Moving Through Water and Liquid Sodium (L. WITTE, J. HESSON, R. O. IVINS, L. BAKER, JR., J. PAVLIK, J. CASSULO, M. SILVERMAN)

In order to analyze adequately the consequences of an incident in a reactor (either fast or thermal) in which hot fuel materials may be dispersed into the liquid coolant, a knowledge of the manner in which large amounts of energy are transferred from these particles to the liquid coolant is needed. At present, neither experimental nor theoretical information is available for the calculation of heat transfer that occurs as small particles at very high temperatures are dispersed in water or liquid sodium. Thus, a study of forced convection film boiling from spheres in both media has been initiated (see ANL-7055, p. 206 and ANL-7125, p. 193).

a. THEORETICAL STUDIES

At present, there is no theoretical solution to the problem of forced convection film boiling from a sphere. This is not surprising since no analytical solution for the flow of a liquid around a sphere in nonboiling flow is now available. The best solution for this single-phase problem is a Blasius-type solution which utilizes a power series representation for the velocity of the liquid around the periphery of the sphere and requires numerical techniques for solution. The film boiling problem is further complicated by both liquid and vapor flowing around the sphere. Also, at present, there is no way to describe the flow phenomenon in the wake region behind the sphere. Therefore, an attempt to describe the problem of film boiling from a moving sphere in mathematical terms has been made.

Bromley²⁶⁻²⁸ et al were the first to attempt to describe the film boiling regime theoretically. They succeeded in solving the case of film boiling in natural convection from a horizontal cylinder. Thermal radiation effects were neglected. The resulting equation for the heat transfer coefficient due to convection only is

²⁶ L. A. Bromley, Chem. Eng. Prog. **46**(5), 221 (1950).

²⁷ L. A. Bromley et al, Ind. Eng. Chem. **45**(12), 2639 (1953).

²⁸ E. I. Motte and L. A. Bromley, Ind. Eng. Chem. **49**(11), 1921 (1957).

very similar to that developed by Nusselt for laminar film condensation on a horizontal cylinder,

$$h_{co} = 0.62 \left[\frac{g \lambda k^3 \rho_v (\rho_l - \rho_v)}{D \mu_v \Delta T} \right]^{1/4} \quad (21)$$

where g is the acceleration of gravity, λ is the latent heat of vaporization, ρ_v is the density of the vapor, ρ_l is the density of the liquid, k is the thermal conductivity, D is the diameter of the cylinder, μ_v is the viscosity of the vapor, and ΔT is the difference between wall temperature and the saturation temperature of the fluid. The effect of thermal radiation is included by writing

$$h = h_{co} + \frac{3}{4} h_r \quad (22)$$

where h is the total heat transfer coefficient and h_r is the coefficient due to thermal radiation. In flows where forced convection predominates over natural convection, Bromley calculated the following heat transfer coefficient, with the constant 2.70 being evaluated from empirical data:

$$h_{co} = 2.70 \left[\frac{k \rho \lambda' U_\infty}{D \Delta T} \right]^{1/2} \quad (23)$$

where U_∞ is the velocity of the fluid stream prior to encountering the cylinder. Bromley also extended this work to include the effects of subcooling in the boiling liquid but the resulting equations were very complex, and the authors state that they should be used only for correlation purposes.

Ellion²⁹ solved the problem for natural convection but proposed a different way to include the effects of thermal radiation. He proposed

$$h = h_{co} \left[\frac{q_{co}}{q_{co} + q_r} \right]^{1/4} + h_r \quad (24)$$

where q denotes heat flux.

McFadden and Grosh,³⁰ Sparrow and Cess,^{31, 32} and

²⁹ M. E. Ellion, "A Study of the Mechanism of Boiling Heat Transfer," JPL Memo 20-88, 1954.

³⁰ P. W. McFadden and R. J. Grosh, "High-Flux Heat

Koh³³ have used the boundary layer treatment of film boiling. McFadden and Grosh solved the problem of natural convection film boiling in a saturated liquid from a vertical flat plate and horizontal cylinder. Sparrow and Cess solved the case of forced convection film boiling from a horizontal flat plate in both a saturated and subcooled liquid. Koh extended the work initiated by McFadden and Grosh.

Hsu and Westwater³⁴ performed an analysis for natural convection film boiling from a vertical surface which provided for transition to turbulent flow at some distance from the leading edge. This theory correlates many experimental data much better than that of Bromley.

Frederking and Clark³⁵ have solved the case of film boiling from a sphere in natural convection. A comparison of data derived from this theory with data taken in liquid nitrogen shows some disagreement. Kobayashi³⁶ has recently attempted to solve the case of forced convection film boiling from a sphere in a saturated liquid. He used the same method as Bromley, but unfortunately the velocity distribution around a cylinder instead of a sphere was used. The effects of thermal radiation were also included in an erroneous manner.

The theory of Kobayashi has been corrected and put in more general form. The results of this correction and generalization can be seen in Figure IV-18. This figure is a plot of $A^{1/2}$ vs. B with C as a parameter. A , B , and C are defined by the following expressions:

$$A^{1/2} = \frac{h_{co}}{k} \left[\frac{8}{3} \frac{R}{U_{\infty}} \frac{\mu}{\rho_l} \right]^{1/2}, \quad (25)$$

$$B = \frac{8}{9} \frac{Rg}{U_{\infty}^2}, \quad (26)$$

and

$$C = \left[\frac{\rho_l k \Delta T}{\rho \mu \lambda'} \right]^{1/2}. \quad (27)$$

B and C are simple functions of flow conditions and physical properties and can be easily calculated for a particular case. Then the value of $A^{1/2}$ can be immedi-

Transfer Studies: An Analytical Investigation of Laminar Film Boiling," ANL-6060, 1959.

³¹ E. M. Sparrow and R. D. Cess, Trans. ASME (Series C) **83**, 370 (1961).

³² E. M. Sparrow and R. D. Cess, Trans. ASME (Series C) **83**, 377 (1961).

³³ J. C. Y. Koh, Trans. ASME (Series C) **84**, 55 (1962).

³⁴ Y. Y. Hsu and J. W. Westwater, Chem. Eng. Prog. Symp. Series, Vol. **56**, No. 30, 1960.

³⁵ T. H. K. Frederking and J. A. Clark, *Advances in Cryogenic Engineering*, Vol. 8, Plenum Press, 1962, p. 501.

³⁶ K. Kobayashi, J. Nucl. Sci. Technol. (Tokyo) **2**(2), 62 (1965).

ately found, and the heat transfer coefficient, h_{co} , can be calculated in turn.

The problem of film boiling from a sphere can be attacked from a boundary-layer viewpoint. Using this type of treatment and matching conditions at the liquid-vapor interface, a differential equation describing the variation of vapor film thickness with angular position on the sphere can be derived.

The model used in this formulation is shown in Figure IV-19. The sphere is considered at rest with the fluid flowing past it. The following assumptions were made:

1. Pure incompressible liquid and vapor.
2. Uniform sphere surface temperature.
3. Constant liquid and vapor physical properties.
4. Smooth liquid-vapor interface.
5. The vapor film thickness is small compared to the radius of the sphere.
6. Inertia effects and energy convection in the vapor film are negligible.
7. Liquid velocity at the liquid-vapor interface is unaffected by vapor drag.
8. The vapor film is transparent to thermal radiation.
9. Liquid-vapor interface is at saturation temperature.

The conservation equations for vapor phase may be written as follows:³⁷

$$\partial \left(\frac{ur}{\partial x} \right) + \partial \left(\frac{vr}{\partial y} \right) = 0 \quad (28)$$

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \frac{\mu}{\rho} \frac{\partial^2 u}{\partial y^2} \quad (29)$$

$$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \quad (30)$$

These are the conservation of mass, momentum, and energy equations, respectively. The pressure is represented by p and α is the thermal diffusivity defined by the ratio $k/\rho C_p$.

The assumption of negligible energy convection in the vapor phase gives a linear temperature distribution in the vapor film.

During film boiling, the sphere is completely enclosed by a blanket of vapor. Therefore, the liquid flowing around the sphere does not feel the influence of the sphere but instead it feels the influence of the vapor blanket. The resistance to flow presented by the vapor film as compared to the solid sphere is very small indeed. If it is postulated that the liquid-vapor interface is in dynamic equilibrium, then the shear stress exerted by the vapor upon the liquid can be assumed to be

³⁷ H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, 4th edition, New York, 1960.

FIG. IV-18. Plot of $A^{1/2}$ vs B for Constant Values of C .

$$\frac{\partial(ur)}{\partial x} + \frac{\partial(vr)}{\partial y} = 0$$

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \frac{\partial^2 u}{\partial y^2}$$

$$u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2}$$

108-9243 T-2

FIG. IV-19. Forced Convection Film Boiling Model for Sphere and Governing Boundary Layer Equations.

equal in magnitude to the shear stress exerted by the liquid upon the vapor. Using Newton's law,

$$\tau_v = \tau_l \quad (31)$$

we may write for the shear stress

$$\tau_v = \mu_v \left(\frac{\partial u}{\partial y} \right) v|_{y=\delta} = \tau_l = \mu_l \left(\frac{\partial u}{\partial y} \right) l|_{y=\delta} \quad (32)$$

where δ is the vapor film thickness. Solving Equation 32

for the velocity gradient in the liquid at the liquid-vapor interface, we find

$$\left(\frac{\partial u}{\partial y} \right) l|_{y=\delta} = \frac{\mu_v}{\mu_l} \left(\frac{\partial u}{\partial y} \right) v|_{y=\delta}. \quad (33)$$

Under normal conditions, the ratio of viscosities is small. In fact, for sodium at saturation conditions and at one atmosphere pressure, the ratio is equal to 0.071. The ratio for water is also quite small. We may say, therefore, that the velocity gradient in the liquid at the liquid-vapor interface is relatively much smaller than the gradient in the vapor. Thus, it can be postulated that the liquid flow approaches that of a frictionless fluid. Since we have assumed that the vapor layer is very thin compared to the sphere radius, we may write for the velocity of the liquid-vapor interface

$$U = \frac{3}{2} U_{\infty} \sin \left(\frac{x}{R} \right). \quad (34)$$

This equation gives the velocity of a frictionless liquid around the periphery of a sphere.³⁷

Solving Equation 29 for the velocity in the vapor and replacing the pressure gradient term by the velocity gradient term from Bernoulli's equation, gives

$$u = \frac{3}{2} U_{\infty} \sin \phi \left[\frac{3}{4} \frac{\rho U_{\infty}}{\mu R} \cos \phi (y\delta - y^2) + \frac{y}{\delta} \right]. \quad (35)$$

Using this and writing an energy balance on an incre-

ment of vapor film, a description of the variation of the vapor film thickness with position on the sphere is determined. It can be said that the heat leaving the sphere surface will be used to form vapor at the liquid-vapor interface and a portion of it will be transferred away from the liquid-vapor interface into the bulk of the liquid which may be at a temperature lower than the saturation temperature of the liquid. The energy leaving the wall has two components, heat due to conduction and heat due to thermal radiation. Therefore,

$$q = q_{\text{cond.}} + q_r = q_{\text{vap.}} + q_b. \quad (36)$$

Substituting known quantities into Equation 36 an equation for the film thickness, δ , is obtained.

$$k \frac{\Delta T}{\delta} + q_r = \frac{3}{2} \frac{\lambda' \rho U_{\infty}}{R \sin \phi} \frac{d}{d\phi} \left[\sin^2 \phi \left\{ \frac{3}{4} \frac{\rho U_{\infty}}{\mu R} \cos \phi \left(\frac{\delta^3}{6} \right) + \frac{\delta}{2} \right\} \right] + q_b. \quad (37)$$

An expression for the heat transferred into the bulk of the liquid, q_b can be written if appropriate assumptions are made.

Using spherical coordinates, assuming axial symmetry, and neglecting conduction in the ϕ -direction as compared to convection in that direction, the differential equation describing the temperature distribution in the liquid around the spherical vapor film becomes

$$u_r \frac{\partial T}{\partial r} + u_{\phi} \frac{1}{r} \frac{\partial T}{\partial \phi} = \alpha \left[\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right] \quad (38)$$

where T is temperature and α is the thermal diffusivity of the liquid. The velocity components, u_r and u_{ϕ} , in light of the assumption of frictionless flow, can be written as,

$$u_r \simeq -3 U_{\infty} \left(\frac{r - R}{R} \right) \cos \phi, \quad u_{\phi} \simeq \frac{3}{2} U_{\infty} \sin \phi. \quad (39)$$

These are obtained directly by differentiating the stream and potential functions for frictionless flow around a sphere.

Sideman³⁸ has shown that if the assumption is made that the heat transfer takes place in a thin layer near the interface, the term $2/r(\partial T/\partial r)$ is negligible in comparison to the term $\partial^2 T/\partial r^2$ in Equation 38. This further implies that the product of the Reynolds number and Prandtl number, called the Peclet number, is much larger than unity. The Reynolds number and Prandtl number are defined by the following equations,

$$\text{Re} = \frac{\rho U D}{\mu}, \quad \text{Pr} = \frac{C_p \mu}{k} \quad (40)$$

where ρ is density, U is velocity, D is the diameter of

the sphere, μ is viscosity, C_p is specific heat capacity, and k is the thermal conductivity of the liquid. Equation 38 now simplifies to

$$u_r \frac{\partial T}{\partial r} + u_{\phi} \frac{1}{r} \frac{\partial T}{\partial \phi} = \alpha \frac{\partial^2 T}{\partial r^2}. \quad (41)$$

The boundary conditions are

$$r = R, \quad 0 < \phi \leq \pi; \quad T = T_{\text{sat}} \quad (42)$$

$$r = \infty, \quad 0 < \phi \leq \pi; \quad T = T_B \quad (43)$$

It is also implied that the penetration of heat into the liquid layer is limited to small distances. The resulting expression for the temperature distribution in the liquid around the sphere is

$$\frac{\Delta T}{\Delta T_B} = \text{erfc} \left[\frac{\psi}{2\sqrt{M\eta}} \right], \quad (44)$$

where

$$\begin{aligned} M &= \frac{2 R \alpha}{3 U_{\infty}} \\ \eta &= \int_0^{\phi} \sin^3 \phi \, d\phi \\ \psi &= y \sin^2 \phi \\ R &= \text{radius of the sphere} \\ U_{\infty} &= \text{bulk velocity} \\ y &= r - R \\ \Delta T &= T - T_B \\ \Delta T_B &= T_{\text{sat}} - T_B \end{aligned}$$

Differentiation of this function will give the heat flux. The resulting expression is

$$\frac{q_b}{A} = k \frac{\Delta T_B}{\sqrt{\pi}} \frac{\sin^2 \phi}{\sqrt{M\eta}} \quad (45)$$

Substituting this into Equation 37 gives

$$\begin{aligned} k_v \frac{\Delta T}{\delta} + q_r &= \frac{3}{2} \frac{\lambda' \rho_v U_{\infty}}{R \sin \phi} \frac{d}{d\phi} \left[\sin^2 \phi \left\{ \frac{3}{4} \frac{\rho_v U_{\infty}}{\mu_v R} \cos \phi \left(\frac{\delta^3}{6} \right) + \frac{\delta}{2} \right\} \right] \\ &+ k_{\ell} \frac{\Delta T_B}{\sqrt{\pi}} \frac{\sin^2 \phi}{\sqrt{M\eta}}. \end{aligned} \quad (46)$$

If Equation 46 could be solved, it would give the variation of the vapor film thickness around the sphere and would include the effects of both thermal radiation and subcooling in the liquid. However, a closed form solution has not been found and numerical methods are required for the solution of the equation.

Nevertheless, a special case of this equation can be solved analytically. If we assume further that there is no subcooling in the liquid, that thermal radiation is negligible, and that a linear velocity profile exists in

³⁸ S. Sideman, Ind. Eng. Chem. **58**(2), 55 (1966).

(Not Drawn To Scale)

308-218 T-1

FIG. IV-20. Knife and Sphere Assembly for Pushing Sphere through Water.

308-216 T-1

FIG. IV-21. Computed Heat Transfer Coefficient from Swinging-Arm Experiments with 1/4-in. dia. Nickel Spheres in Water. (Velocity of Sphere = 12.7 ft/sec.)

the vapor film, Equation 46 is greatly simplified and can be solved in closed form. If the vapor film is assumed to separate from the sphere surface at the 90° point on the sphere, then the heat-transfer coefficient for a sphere moving through a liquid and causing film boiling is

$$h_{co} = 0.698 \left[\frac{k\rho\lambda'U_{\infty}}{D\Delta T} \right]^{1/2} \quad (47)$$

This is strikingly similar to the coefficient derived by Bromley for forced convection film boiling around a horizontal cylinder. At present, no saturated film boiling data from a sphere is available to compare with data derived from this theory.

Further work is being planned to obtain data in a saturated liquid to test the applicability of the theory developed above.

b. EXPERIMENTAL INVESTIGATION IN WATER

Transient heat transfer experiments, in which a heated nickel ball is passed rapidly through a pool of water, are continuing. The experimental apparatus, which is described in detail in ANL-7055, p. 206, and ANL-7125, p. 193, consists of a swinging arm (or pendulum) with a knife blade attached to the arm. In the previous work, the sphere was pulled through the water. In the most recent work, reported herein, the sphere was pushed through the water. This was accomplished by welding one lead of a Pt/Pt-10% Rh thermocouple to each side of the sphere and then attaching a central stiff wire to the sphere as shown in Figure IV-20.

Runs were made with a nickel sphere in water at 23°C (room temperature) and at 60°C. In all runs, the path length was kept constant at ~21.6 in. The velocity varied very slightly between 12.66 and 12.75 ft/sec. The data were then subjected to the computer program described in ANL-7125, p. 195, which yielded results in terms of average heat transfer coefficient and average heat flux as a function of the average surface temperature of the sphere. The average surface temperature of the sphere ranged from approximately 900°C down to 100°C.

In Figures IV-21 and IV-22, the average heat transfer coefficient (h) is plotted vs. the average surface temperature of the sphere. In both figures, a comparison is made with the earlier data obtained from a sphere pulled through the water. As can be seen from Figure IV-21, the curves for room temperature water correspond closely except for the points occurring at

308-213 T-1

FIG. IV-22. Computed Heat Transfer Coefficient from Swinging-Arm Experiments with 1/4-in. dia. Nickel Spheres in Water. (Velocity of sphere = 12.7 ft/sec.)

220 and 318°C. These two points indicate a very sharp peak in the heat transfer coefficient which was not seen in the earlier results.

In Figure IV-22, for 60°C H₂O, there is close agreement above 500°C. However, at temperatures below 500°C there is again a very sharp peak which was not noted in the previous measurements.

308-215 T-1

FIG. IV-23. Computed Heat Fluxes from Swinging-Arm Experiments with 1/4-in. dia. Nickel Spheres in Water. (Velocity of sphere through water = 12.7 ft/sec.)

In Figure IV-23, the average heat flux (q/A), plotted as a function of average surface temperature is compared with the earlier data using a sphere pulled through the water. In the lower temperature water (23°C), a peak at ~250°C is evident which was not indicated by the data with the pulled sphere. With 60°C water, the peak, which did occur with the pulled sphere, is much sharper and occurs at lower temperatures. In both cases (23°C and 60°C H₂O), there is fairly close agreement above 500°C. The difference in the results is probably the result of differences in the fluid flow pattern around the pushed and pulled spheres.

In future work on transient boiling studies in water, a motorized swinging arm apparatus will be used. This will permit not only variable path lengths, but also variable velocities.

c. EXPERIMENTAL INVESTIGATION IN SODIUM

The experimental investigation of forced convection film boiling from a sphere to liquid sodium has been continued. It is felt that in a power excursion incident the temperature of the dispersed material will be high enough so that film boiling of the liquid sodium will occur. The apparatus, which was previously described in ANL-7125, p. 197, is shown in Figure IV-24. The semicircular tank for holding the molten sodium has

108-9858 T-1

FIG. IV-24. Sodium Heat Transfer Apparatus.

a radius of 10 in. and is 4 in. wide. The d-c motor which drives the swinging arm has its armature windings "printed" upon a thin ceramic disc. Consequently, it has extremely low inertia and accelerates to top speed very rapidly. Attached to the motor shaft directly over the sodium tank is a 1/2-in. dia. tantalum sphere welded to a 1/8-in. OD tantalum tube; the distance from the motor shaft to the sphere can be varied. Extending through the support tube and into the sphere is a 1/16-in. OD, tantalum-clad, BeO-insulated W-5% Re/W-26% Re thermocouple (see Figure IV-25). This thermocouple is welded to the bottom of a hole drilled to within 0.032 in. of the surface of the sphere.

In Figure IV-24 the sphere is positioned beneath a single-turn copper induction coil used to heat the sphere. Sphere temperatures above 2000°C can be obtained using this induction heater.

After the sphere has been heated to the desired temperature, the motor is actuated and the sphere moves out of the induction coil and through the liquid sodium. Since the acceleration of the motor is very rapid, the sphere moves through the sodium pool with a constant linear velocity.

The temperature history of the sphere as it moves through the sodium pool is recorded with a Honeywell-Hieland Visicorder. The velocity and temperature of the sphere are displayed upon the Visicorder record simultaneously. This is done with the use of a perforated timing wheel attached to the back of the motor shaft. The wheel separates a light source and a photoconductive cell; as the wheel turns, light intermittently falls upon the photo cell and a blip occurs on the record. Both angular velocity and acceleration can then be calculated from the record, and since the distance from the motor shaft to the sphere is known,

108-9412 T-2

FIG. IV-25. Thermocouple, Sphere, Support Tube Assembly.

308-206 T-1

FIG. IV-26. Temperature-Time Trace for 1/2-in. Tantalum Sphere Moving through Sodium. (Run 7, velocity = 10.35 ft/sec.)

the linear velocity of the sphere can be calculated. The sphere velocity can be varied from approximately 3 to 15 ft/sec.

Because of the necessity for containing the entire apparatus in an argon atmosphere glovebox, a system has been built to provide remote control for the motion of the sphere through the sodium. The following modes of operation are possible with the system.

1. Relatively fast motion of the sphere from the induction heater, through the sodium pool, to rest above the sodium pool (data run).
2. Relatively slow motion back through the sodium pool to the induction heater.
3. Relatively slow motion back through the sodium pool to a position outside the induction heater.
4. Slow motion from the position described in (3) to the induction heater.

The sodium is heated from below by electrical resistance heaters and sodium temperatures up to 500°C can be easily attained. The sphere temperature will be varied from approximately 900 to >2000°C. All data will be taken with this apparatus at near atmospheric pressure because of the limitations of the glovebox.

A computer program that utilizes the technique developed by Stolz³⁹ for the solution of the inverse problem of heat conduction has been developed for treatment of the data from these experiments. In this program, the measured temperature-time history of a point near the surface of the sphere, such as that shown in Figure IV-26, is used as input to calculate the heat flux at the surface of the sphere and the sphere surface temperature. (In contrast, the computer technique used in the heat transfer experiments in water calcu-

³⁹ G. Stolz, Trans. ASME (Series C) **82**, 20 (1960).

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FIG. IV-27. Surface Temperature and Heat Flux vs Time for $\frac{1}{2}$ -in. Tantalum Sphere Moving through 300°C Sodium. (Run 7, velocity = 10.35 ft/sec)

lates a heat transfer coefficient based on an average sphere temperature.)

Figure IV-27 shows the calculated surface temperature versus time. From these results, the surface heat flux versus surface temperature can be calculated; the results for the case shown in Figure IV-26 are plotted in Figure IV-27 as the discrete points. The calculated heat flux at the highest surface temperature includes the portion of the experimental time when the sphere first enters the sodium pool. Consequently, the flow has not fully developed around the sphere and the first heat flux data point appears quite low in comparison to the points taken as the sphere moves progressively through the sodium pool. This point also represents the first calculation in the transient data reduction technique. It is a characteristic of transient heat transfer analyses for the computation of the first time point to be quite low. However, as the calculation proceeds forward in time, the transient analyses yielded more accurate values. The dotted line in Figure IV-27 represents a smoothing of the heat flux data. Figure IV-28 shows data for several experimental runs which have been corrected in this manner.

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FIG. IV-28. Heat Flux vs Surface Temperature for $\frac{1}{2}$ -in. dia. Tantalum Sphere Moving through 300°C Sodium.

The data in Figure IV-26 include temperature measurements after the sphere has exited from the sodium. For comparison, a cooling curve for a 1/2-in. dia. tantalum sphere cooling in argon was measured. This cooling process is relatively slow and the sphere can be assumed to be at a uniform temperature with little error. As shown in Figure IV-26, a sphere rapidly approaches this type of equilibrium cooling after it exits from the sodium. By finding the point on the temperature trace where the slope first matches that of the cooling curve for cooling in argon only, the equilibrium point may be found. By projecting the cooling curve in argon backwards in time, the amount of cooling that the sphere underwent from the time it exited from the sodium to the time it reached equilibrium can be closely estimated. This also provides a method of calculating the total energy decrease in the sphere owing to its encounter with the liquid sodium. The total energy change is simply the change in enthalpy of the sphere as it passes through the sodium. The energy transferred to the argon can be found as described previously. The remaining part of the energy decrease during the time between entry of the sphere into the sodium pool and the attainment of equilibrium after leaving the sodium pool must have been transferred into the sodium. The time that the sphere remained in the sodium pool can be calculated from velocity and sodium liquid level measurements.

The average heat transfer rate can be found by the relation

$$\left(\frac{q}{A}\right)_{\text{avg.}} = \frac{\Delta H}{\Delta t A} \quad (48)$$

where $(q/A)_{\text{avg.}}$ is the average heat transfer rate, ΔH is the change in enthalpy, Δt is the time in the sodium,

and A is the area of the sphere. The average heat transfer rate is independent of thermocouple response. Even if good thermocouple response cannot be obtained, this technique will still give basic information on the heat transfer rate. This is the technique currently used in the experiments with water. However, an average heat flux must apply at an average sphere temperature rather than at a sphere surface temperature. Therefore, this technique will not provide the detailed information that can be calculated if the thermocouple responds properly.

The above technique provides a very convenient check on the accuracy of the calculated heat flux using the transient technique. The computer-calculated heat flux can be integrated and compared with the heat flux found from equilibrium considerations. This has been done for Run 7. The average heat flux calculated from equilibrium considerations for this case is 509 cal/(cm²)(sec). The integrated mean value using the computer-calculated points is 408 cal/(cm²)(sec). This represents a 20% variation. The integrated mean value for the smoothed heat flux shown in Figure IV-27 is 430 cal/(cm²)(sec). This represents a variation of approximately 15% which is in good agreement for transient heat transfer measurements.

A plot of the raw data such as that in Figure IV-26 is also valuable in showing whether the thermocouple imbedded in the sphere is responding to the temperature transient as it should. That the response of the sphere thermocouple for Run 7, shown in the figure is adequate can be seen by the small amount of time that it takes to achieve the equilibrium temperature of the sphere.

It is expected that the preliminary data described above will be extended considerably during the next reporting period.

3. High Temperature Physical Properties: Heat Capacity of Liquid UO₂ (L. LEIBOWITZ, L. W. MISHLER)

A program has been initiated to measure the high temperature heat capacity of UO₂ (see ANL-7125, p. 198), because of the importance of that quantity in fast reactor safety calculations. The general approach will be to encapsulate the UO₂ in tungsten, heat by induction, and measure the heat content by conventional drop calorimetry. Although calculations show cooling curve methods to be less likely to succeed than the method outlined above, a few experimental tests of the cooling curve methods will also be made. It is hoped that temperatures from the melting point of UO₂ (2800°C) to near the melting point of tungsten (~3400°C) can be explored.

As was reported previously (ANL-7125, p. 198), the initial work consisted of tests of the suitability of tungsten as an encapsulation material at temperatures significantly above the melting point of UO₂. Tests have been carried out using a wide variety of sources of tungsten and in no case was any gross attack of the container by the UO₂ observed. The capsules, after heating, were cut open, polished, and examined metallographically. In many cases a metallic precipitate was seen in the oxide. One example of this deposit shown in Figure IV-29. The capsule for this experiment was made from wrought tungsten tubing and the encapsulated material was heated to about 3350°C

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FIG. IV-29. Section of Tungsten Capsule Containing UO_2 after Heating to 3350°C for 1 to 2 Minutes.

a. Tungsten (present as bright areas)

b. Uranium (present as bright areas)

100 μ

308-198 T-1

FIG. IV-30. Tungsten and Uranium X-Ray Emission Patterns of a Portion of Figure IV-29.

for one to two minutes. Metallographic examination indicated that the precipitated material was tungsten; however, positive identification was made by electron microprobe analysis.⁴⁰ In Figure IV-30 are shown the tungsten and uranium X-ray patterns from the central region of the view shown in Figure IV-29. The bright areas of Figure IV-30a show the location of tungsten; it is clearly confined to the dendritic precipitate. The dark background shows the absence of

tungsten in the UO_2 matrix. In Figure IV-30b, in which bright areas indicate the location of uranium, it is clear that there is no appreciable uranium in the dendrite.

A chemical analysis of this residue showed the presence of only 1.1 w/o tungsten. The area selected in Figure IV-29 is atypical, i.e., the concentration of tungsten is greater than the average concentration. In other experiments, it was observed that the amount of tungsten in the residue decreased as the maximum

⁴⁰ This analysis was performed by N. Stalica.

temperature reached was decreased. Further analyses of test capsules are in progress.

The material from the experiment at 3350°C was also analyzed to determine whether or not the O:U ratio had changed during heating. No change from the initial composition of $\text{UO}_{2.00}$ was detected.

Almost all the equipment needed for carrying out

the heat capacity measurements has been ordered, and design and construction of the vacuum chamber in which the heating will be carried out has begun. In addition, capsules of various shapes are being fabricated to achieve uniformity of heating. Several capsule types will be tested before a final choice is made.

4. Fuel Migration Studies (M. G. CHASANOV, D. F. FISCHER)

A program is being carried out to determine the extent of fuel migration and segregation in mixed uranium-plutonium fuels. A significant degree of segregation might seriously decrease the effect of Doppler broadening as a shut-down mechanism in an operating reactor. An investigation of migration in mixed fuels such as uranium and plutonium oxides, carbides, and nitrides in a thermal gradient is planned. Segregation within fuel samples will be determined by chemical, metallographic, and electron microprobe analyses.

A vacuum system suitable for use with a gradient furnace in a plutonium glovebox has been built and tested. The apparatus is shown in Figure IV-31. The gradient furnace located in the bell jar consists of (1) a resistance-heated tungsten foil which heats the upper end of a sample to temperatures above 2000°C and (2) a water-cooled base plate to maintain a thermal gradient of 600 to 800°C between the upper and lower ends of the sample. Heat shields surround the sample,

foil, and base plate. Temperatures are measured by W-5% Re/W-26% Re thermocouples.

Initial experiments in development of the furnace utilized tantalum foils as heaters. Examination of a cross section of a UO_2 pellet that was heated for 32 minutes under the temperature gradient described above showed a deposit of tantalum and metallic-appearing inclusions distributed in the oxide. Electron microprobe analysis identified these inclusions as either uranium metal or oxygen-deficient UO_2 . Subsequent experiments indicated that tungsten foils were more reliable than tantalum foils in the gradient furnace. For long-term application tungsten-mesh heaters may be employed.

At the present time, extended-use tests of the apparatus, employing ceria-urania pellets and tungsten foil heaters, are proceeding satisfactorily. Upon successful completion of these tests, the apparatus will be installed in a plutonium glovebox.

FIG. IV-31. Gradient Furnace Vacuum System for Use in Fuel Migration Studies.

5. Sodium-Air Reactions (L. LEIBOWITZ)

Rational safety analyses for fast reactors require knowledge of the temperatures and pressures generated during sodium combustion in air. Combustion of both pools and sprays of sodium will have to be considered. Baker and Tevebaugh (ANL-7055, p. 208) pointed out that regardless of the burning mechanism, the pressures and temperatures are limited by

TABLE IV-7. COMPARISON OF THE BAKER AND TEVEBAUGH (B-T) AND FREE ENERGY MINIMIZATION (FEM) CALCULATIONS OF ADIABATIC PRESSURES AND TEMPERATURES FOR SODIUM-AIR REACTION

Initial Conditions: Air, 12.2 psia, 25°C; Sodium, 427°C, liquid

Z, Sodium-Oxygen Ratio (g atom Na/mole O ₂)	Adiabatic Temperature (°C)		Total Pressure (atm)	
	B-T	FEM	B-T	FEM
1	1257	1259	4.18	4.18
2	1707	1689	5.40	5.34
4	1902	1918	6.35	6.53
5	1947	1943	7.05	7.04
6	1877	1863	7.49	7.47
7	1660	1607	7.77	7.57
Air initially at 14.7 psia				
4	1930	1943	7.47	7.68

the thermodynamic properties of the system. Calculations have been carried out for equilibrium conditions in sodium-air and sodium-air-water mixtures using a computer program designed to minimize free energy.

The method used is that originated by White, Johnson, and Dantzig⁴¹ and extended by Oliver, Stephanou, and Baier⁴² to include condensed phases. The computer program⁴³ was designed to use thermodynamic data from the JANAF⁴⁴ tables. Briefly, the equilibrium distribution of species in a system of fixed elemental composition is determined at a specified pressure (or volume) and temperature by minimizing free energy subject to chemical balance constraints. At constant pressure, the Gibbs free energy is minimized, while at constant volume, the Helmholtz free energy is minimized. (This is an extension of the work reported by Oliver, Stephanou, and Baier;⁴² they de-

scribe only constant pressure calculations.) The equilibrium temperature is then found from a heat balance assuming adiabatic conditions. The composition of the mixture at the equilibrium temperature can then be computed by interpolating the thermodynamic data to find the composition giving the minimum free energy at that temperature.

TABLE IV-8. CALCULATED ADIABATIC TEMPERATURES AND PRESSURES FOR SODIUM-AIR REACTION

Initial Conditions: Air, 14.7 psia, 25°C; Sodium, 427°C, liquid

Z, Sodium-Oxygen Ratio (g atoms Na/mole O ₂)	Adiabatic Temperature (°C)	Partial Pressure (atm)				Total Pressure (atm)
		N ₂	O ₂	NaO	Na	
1	1292	4.15	0.82	0.00	0.00	4.97
2	1729	5.31	0.73	0.10	0.21	6.35
3	1882	5.71	0.50	0.21	0.69	7.11
4	1961	5.92	0.26	0.27	1.32	7.78
5	1987	5.99	0.08	0.22	2.11	8.40
6	1901	5.76	0.00	0.06	3.12	8.94
7	1634	5.05	0.00	0.01	4.02	9.08
8	1335	4.26	0.00	0.01	4.53	8.80

TABLE IV-9. CALCULATED ADIABATIC TEMPERATURES AND PRESSURES FOR SODIUM-AIR-WATER REACTION

Initial Conditions: Air, 14.7 psia, 25°C (saturated with H₂O); Sodium, 427°C, liquid

Z, Sodium-Oxygen Ratio (g atoms Na/mole O ₂)	Adiabatic Temperature (°C)	Partial Pressure ^a (atm)					Total Pressure (atm)
		N ₂	O ₂	NaO	Na	NaOH	
1	1177	3.72	0.67	0.00	0.01	0.30	4.70
2	1766	5.24	0.61	0.05	0.12	0.42	6.44
3	1889	5.56	0.41	0.08	0.67	0.45	7.17
4	1901	5.59	0.22	0.08	1.41	0.45	7.75
5	1836	5.42	0.08	0.05	2.25	0.44	8.24
6	1576	4.75	0.05	0.02	3.11	0.38	8.31
7	1294	4.03	0.03	0.01	3.66	0.32	8.05

^a Equilibrium pressures of H₂ and H₂O were each less than 0.005 atm.

A free energy minimization computer program was developed and first used to repeat the calculation reported by Baker and Tevebaugh. Briefly, their method consisted of finding the compositions which simultaneously satisfied equilibrium constants and the material balance equations. The equilibrium adiabatic temperature was found graphically using an energy balance similar to that used here. The initial composition of the mixture was 4 moles N₂, 1 mole O₂, and Z

⁴¹ W. B. White, S. M. Johnson, and G. B. Dantzig, J. Chem. Phys. **28**, 751 (1958).

⁴² R. C. Oliver, S. E. Stephanou, and R. W. Baier, Chem. Eng. **69**(4), 121 (1962).

⁴³ The program was prepared by J. L. Anderson, Applied Mathematics Division, ANL.

⁴⁴ JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, 1965.

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FIG. IV-32. Calculated Equilibrium Temperatures for the Sodium-Air Reaction.

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FIG. IV-33. Calculated Equilibrium Pressures for the Sodium-Air Reaction.

TABLE IV-10. CALCULATED MAXIMUM ADIABATIC TEMPERATURES AND PRESSURES FOR SODIUM-AIR REACTION.

Initial Water Content of Air	Peak Temperature (°C)	Sodium-to-Oxygen Ratio at Peak Temperature (g atoms Na/mole O ₂)	Peak Pressure (atm)	Sodium-to-Oxygen Ratio at Peak Pressure (g atoms Na/mole O ₂)
0	1987	5	9.08	7
Saturated at 25°C	1901	4	8.31	6

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FIG. IV-34. Equilibrium Temperatures for the Sodium-Air Reaction.

gram atoms of Na. The sodium was taken to be initially at 700°K, while the N₂ and O₂ were at 298°K. The species existing at equilibrium were N₂, O₂, Na(g), NaO(g), and Na₂O(l). Almost all the calculations were done at 12.2 psia with a value for the volume of 143 liters. A comparison of results from the computer with those from the hand calculations of Baker and Tevebaugh⁴⁵ is shown in Table IV-7. Very good agreement was found, as was expected.

⁴⁵ In Equation 8 of Baker and Tevebaugh (ANL-7055, p. 209), the denominator of the second term on the left hand side

Since the values of equilibrium temperature and pressure are to be used in conjunction with safety analyses, the computer calculation was repeated using an initial pressure of 14.7 psia and a nitrogen-to-oxygen ratio more truly representative of air (3.7733). The calculation was done for dry air, and for air saturated with water at 25°C. The results of these calculations are shown in Tables IV-8 and IV-9. The entire calculation was repeated with NaO formation excluded. The equilibrium temperatures and pressures are plotted in Figures IV-32 and IV-33. The effect of NaO formation is small; the largest change noted by excluding NaO was an increase of 40°K for a ratio of sodium to oxygen of 5 with dry air.

The species considered to be present when water was added were, in addition to those already noted, $H_2(g)$, $H_2O(g)$, and $NaOH(g)$.⁴⁶ The calculations showed that virtually all of the hydrogen initially present in the water was found in the NaOH.

The maximum pressures and temperatures thermodynamically possible are not very different from those given by Baker and Tevebaugh. The values for dry air and for air saturated with water at 25°C with NaO formation are summarized in Table IV-10. The added water has the effect of lowering both the maximum temperature and the maximum pressure attainable.

It is interesting to compare these calculations with those of other workers. In Figures IV-34 and IV-35, results of these calculations (for the case of dry air with NaO present) are compared with those of Humphreys,⁴⁷ and Garelis and Nims.⁴⁸ Agreement is fairly good between the values of Garelis and Nims and those calculated here. Differences in the sodium-to-oxygen ratio, volume, and thermodynamic data appear to be responsible for the differences found. In the

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FIG. IV-35. Equilibrium Pressures for the Sodium-Air Reaction.

case of Humphreys' calculation, the source of the large differences lies in Humphreys' assumption of complete reaction. Our calculation shows that complete reaction does not occur, particularly at higher temperatures. Indeed, for a sodium-to-oxygen ratio of 4, a stoichiometric mixture for formation of Na_2O , 21.1% of the sodium initially present is found as $Na(g)$ at equilibrium.

The chief experimental effort, thus far, in the study of sodium-air reactions is the development of equipment for the study of the reaction of sodium sprays in air. Pressure generation rates, extent and rate of reaction, and the nature of the oxide products are variables that will be examined. A pneumatically operated piston device suitable for spraying about 15 g of molten sodium into an air-filled enclosure has been constructed and is currently being tested with water. When construction of dry box facilities is completed, experimental work will begin using sodium.

was inverted in error. The correct equation, which was actually used in their calculations, is,

$$P_{(Na)} + \frac{4 - Z}{(V/RT)} = \frac{K_1}{K_2} \frac{1}{P_{(Na)}} + \frac{4K_1^2}{P_{(Na)}^4}$$

⁴⁶ No new condensed phases needed to be considered over the range of sodium-to-oxygen ratios under investigation.

⁴⁷ J. R. Humphreys, Jr., "Sodium-Air Reactions as They Pertain to Reactor Safety and Containment", *Proc. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva, 1958*, Vol. 11, p. 177.

⁴⁸ E. Garelis and J. B. Nims, "Sodium-Air Accident Study for a Sodium Cooled Reactor", AECU-4161 (1959).

C. METAL OXIDATION AND IGNITION KINETICS

1. Burning Tests with Uranium-Plutonium-Molybdenum and Uranium-Plutonium-Titanium Ternary Alloys (L. BAKER, JR., D. F. FISCHER)

Several brief series of burning experiments were performed with ternary alloys containing uranium, plutonium, and small quantities of either molybdenum or titanium. The alloys are typical of compositions under consideration for use in critical experiments in facilities such as ZPR-III, ZPR-VI, and ZPPR.

The experimental program was not intended to be a comprehensive study of the oxidation, ignition, and burning characteristics of the alloys under consideration. Instead, the experiments were designed to determine whether self-sustaining or propagating combustion could be induced in freely suspended, unclad plates.

a. EXPERIMENTAL

Sample plates were either squares (0.5 by 0.5 in.) or rectangles (2 by 0.5 in.) and varied in thickness from 0.12 to 0.20 in. All experiments were performed in atmospheric air at a relative humidity ranging between 24 and 48%. Samples were heated rapidly by induction to a temperature of from 600 to 1100°C. Induction power was turned off when the predetermined temperature was reached. The square samples were heated uniformly to determine if the air oxidation reaction was self-sustaining. The rectangular samples were heated only at the lower end to determine if the reaction was propagating. Thermocouples were used to follow the temperature-time history of the samples. Postheating examination of the samples included an approximate determination of the extent of oxidation.

Three alloys having the following nominal compositions were studied:

- U, 19.6 w/o Pu, 2.5 w/o Mo (SEFOR material)
- U, 25 w/o Pu, 2.5 w/o Mo
- U, 25 w/o Pu, 3 w/o Ti

Specimens having the first composition (U, 19.6 w/o Pu, 2.5 w/o Mo) were obtained from SEFOR plate material made by the Nuclear Metals Corp. These plates were made by casting in a yttria-coated graphite mold. SEFOR plate specimens designated as having a low carbon content contained between 160 and 310 ppm carbon while specimens designated as having a high carbon content contained between 760 and 1130 ppm carbon.

Specimens having the high plutonium content (25 w/o) were prepared in two separate groups. The first

group⁴⁹ was made up of plate samples nominally 0.12 in. in thickness. These alloys were prepared by arc melting several times. They were then remelted in an induction furnace and cast in a chilled copper mold. The surfaces of the samples were as-cast. The second group⁵⁰ was made up of alloy plates nominally 0.20 in. in thickness. The alloys were analyzed and found to contain 400 to 600 ppm carbon.

All of the specimens were fabricated from the appropriate plate material by machining to the approximate

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FIG. IV-36. Test Specimens with Thermocouple Wells. (Dimensions in inches.)

size 0.5 by 0.5 in. or 2 by 0.5 in. One thermocouple hole was drilled in the smaller samples, and two were drilled in the larger samples in the locations indicated in Figure IV-36. The thermocouple holes were drilled by the Elox method in a nitrogen hood. Each specimen was ultrasonically cleaned in alcohol, dried, and weighed.

The experiments were performed in an air-filled glovebox. A single-turn induction coil, shown in Figure IV-37, was connected through a gloveport to a 4-kw Reeve Electronic Generator which was located outside the glovebox. The induction coil was 0.5 in. in depth

⁴⁹ Prepared by L. Kelman and H. Rhude of the Metallurgy Div., ANL.

⁵⁰ Prepared by A. Shuck and H. Jelinek of the Metallurgy Div., ANL.

so that it completely enclosed the 0.5 by 0.5 in. specimen plates. The 2 by 0.5 in. specimens were mounted vertically so that only the lower 0.5 in. of each specimen was enclosed within the coil as shown in Figure IV-37. The induction coil and leads were water-cooled; thus they were not perceptibly heated during the experiments.

Specimens were mounted on the end of a vertical alumina tube. The lower specimen thermocouple passed through the tube and entered the lower thermocouple hole in the specimen. The thermocouple helped to support the sample. The mounting arrangement prevented contact between the surface of the induction coil and the specimen. The thermocouples were 28-gauge chromel-alumel bare junction thermocouples and were positioned within the specimens as shown in Figure IV-36. Thermocouple output was recorded continuously on a strip chart recorder.

To begin an experiment, the induction power was set at a relatively high level, and switched on. Power was turned off abruptly when the thermocouple output on the recorder indicated that the desired maximum specimen temperature had been reached. A clock, which was electrically coupled to the induction generator, indicated the heating time. Heating time required to reach a given temperature varied widely because of differences in specimen size, coil arrangement, and induction power setting.

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FIG. IV-37. View of Induction Coil with Propagation Test Specimen in Position.

After an experiment, the specimen was polished until approximately 50% of the surface had the appearance of shiny metal. The specimen was then weighed. The weight loss was taken to be the amount of metal which had been oxidized during the experiment. The results were reported as percent of metal reacted.

b. RESULTS OF IGNITION SUSTAINING EXPERIMENTS

Experiments designed to determine whether self-sustaining combustion could be initiated were performed with the nominal 0.5 by 0.5 in. plates. The results (extents of reaction) are given in Table IV-11 (column 5). Control experiments were performed with stainless steel plates and normal uranium plates. Experiments with stainless steel plates showed that inert metal specimens could be heated to temperatures of about 700 to 1100°C in 0.3 to 0.5 min; after the power was shut off, the specimens cooled to 200°C in a total time of 3 to 4 min from the initiation of the experiment. An experiment with a uranium specimen showed that sustained combustion was not initiated. The uranium sample was heated to 912°C in 0.30 min; it cooled to 200°C in 2.6 min; the extent of reaction during the heating-cooling cycle was 5.7%.

The initial series of experiments with the uranium-plutonium ternary alloy plates was designed to bring the specimen temperatures to values approaching the liquidus temperature. No sustained reaction was induced by heating in the range 900 to 1200°C for the molybdenum-containing alloys. The extents of reactions occurring during the heating-cooling cycle ranged from 9.7 to 11.1% for the 0.12 in. thick samples and from 5.0 to 7.3% for the 0.20 in. thick samples. A typical temperature-time trace from one of these experiments is shown in Figure IV-38. The appearance of a specimen before and after an experiment is shown in Figure IV-39 (A and B). There was no apparent effect of plutonium content in the range 19.6 to 25 w/o plutonium or of carbon content for the molybdenum-containing alloys reported in Table IV-11.

The experiments with the titanium-containing alloy in which the specimens were heated into the range 940 to 1020°C resulted in somewhat more extensive reaction than that which occurred with the molybdenum-containing alloys. The extent of reaction was 17.1% for a 0.12-in. thick titanium alloy sample and varied between 6.5 and 7.7% for 0.20-in. thick samples. Typical temperature-time curves for these titanium-containing alloy plates were very similar to that for the molybdenum-containing alloy plate shown in Figure IV-38. The appearance of a specimen before and

TABLE IV-11. BURNING TEST EXPERIMENTS WITH URANIUM-PLUTONIUM-MOLYBDENUM AND URANIUM-PLUTONIUM-TITANIUM TERNARY ALLOYS

Sample Dimensions (in.)	Induction Heating Time (min)	Maximum Sample Temperature (°C)		Percent Reaction		Time at Which Specimens had Cooled to 200°C (min)
		Bottom End	Top End	Sustaining Experiment	Propagation Experiment	
Control Samples, Stainless Steel						
0.5 × 0.5 × 0.12	0.50	1006	—	—	—	3.5
0.5 × 0.5 × 0.12	0.30	726	—	—	—	3.2
0.5 × 0.5 × 0.25	0.35	1087	—	—	—	4.1
0.5 × 0.5 × 0.25	0.35	760	—	—	—	4.0
2.0 × 0.5 × 0.12	1.00	1064	306	—	—	4.5
2.0 × 0.5 × 0.12	0.50	833	200	—	—	2.9
2.0 × 0.5 × 0.25	0.35	942	245	—	—	3.9
2.0 × 0.5 × 0.25	0.40	686	175	—	—	2.8
Control Samples, Normal Uranium						
0.5 × 0.5 × 0.12	0.30	912	—	5.7	—	2.6
2.0 × 0.5 × 0.12	0.50	936	330	—	1.3	2.4
U, 19.6 w/o Pu, 2.5 w/o Mo (SEFOR Material)						
0.5 × 0.3 × 0.13	0.26	1027	—	11.1	—	3.3
0.5 × 0.5 × 0.20 ^a	0.25	1117	—	5.6	—	4.2
0.5 × 0.5 × 0.19 ^b	0.25	1016	—	5.8	—	3.7
0.5 × 0.5 × 0.20 ^a	0.21	979	—	5.0	—	4.6
0.5 × 0.5 × 0.20 ^a	0.58	655	—	100	—	~45
0.5 × 0.5 × 0.19 ^b	0.82	637	—	100	—	~60
2.0 × 0.5 × 0.13	0.37	954	—	—	1.8	2.3
2.0 × 0.5 × 0.13	0.35	907	208	—	1.4	2.4
2.0 × 0.5 × 0.13	0.30	740	190	—	0.7	2.1
1.7 × 0.5 × 0.19 ^b	0.35	984	330	—	1.6	3.7
2.0 × 0.5 × 0.21 ^a	0.35	876	271	—	1.1	4.0
U, 25 w/o Pu, 2.5 w/o Mo						
0.5 × 0.5 × 0.12	0.30	1174	—	9.7	—	4.1
0.5 × 0.5 × 0.22	0.35	993	—	7.3	—	4.5
0.5 × 0.5 × 0.22	0.21	958	—	6.3	—	4.7
0.5 × 0.5 × 0.22	2.00	647	—	100	—	~50
2.0 × 0.5 × 0.12	0.30	931	605	—	100	—
1.8 × 0.5 × 0.22	0.35	980	396	—	1.9	4.5
1.8 × 0.5 × 0.22	0.50	920	340	—	1.1	4.7
1.8 × 0.5 × 0.21	0.25	904	263	—	1.5	3.6
1.8 × 0.5 × 0.21	0.50	895	352	—	1.9	4.5
1.8 × 0.5 × 0.22	0.41	850	210	—	2.3	3.1
U, 25 to 28 w/o Pu, 3 w/o Ti						
0.5 × 0.5 × 0.12	0.30	1020	—	17.1	—	4.5
0.6 × 0.5 × 0.20	0.25	1010	—	7.7	—	5.6
0.5 × 0.5 × 0.21	0.22	952	—	6.2	—	5.0
0.6 × 0.5 × 0.21	0.35	943	—	6.5	—	5.2
0.6 × 0.5 × 0.19	11.0	692	—	100	—	~205
1.1 × 0.5 × 0.12	0.30	1006	532	—	8.4	4.4
1.8 × 0.5 × 0.20	0.35	1010	360	—	2.0	4.6
1.8 × 0.5 × 0.21	0.31	972	393	—	1.5	4.7
1.8 × 0.5 × 0.21	0.60	952	401	—	1.8	4.8

^a Low carbon content (160-310 ppm).^b High carbon content (760-1130 ppm).

After an experiment is included in Figure IV-39 (D and E).

A second series of experiments was performed in which specimens were heated to maximum temperatures in the range 600 to 700°C. These experiments invariably resulted in a self-sustained reaction which persisted until the specimens were completely oxidized. A typical temperature-time curve for a molybdenum-containing alloy is shown in Figure IV-40 and the appearance of the completely oxidized residue is shown in Figure IV-39C. In the temperature-time curve shown in Figure IV-40, the induction power was turned off when the sample reached 655°C. The sample temperature then decreased to about 615°C and rose spontaneously to about 645°C. The sample then oxidized to completion in 50 to 60 min. The apparent gradual decrease in sample temperature was probably due to poor physical contact between the thermocouple and the metal because of the oxide growth. Finely divided oxide powder fell from molybdenum-containing alloy samples at an apparently constant rate throughout the reaction. The dull red color of the underlying metal appeared, visually, to be unchanged throughout the 50 to 60-min reaction period, suggesting that the temperature remained reasonably constant in the range 600 to 660°C. A small quantity of smoke emanated from the reacting specimens. The smoke was probably volatile MoO_3 .

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Fig. IV-38. Typical Temperature-Time Trace for a U, 20 w/o Pu, 2.5 w/o Mo Specimen (0.5 by 0.5 by 0.2 in.): No Sustaining Reaction in Air.

The titanium-containing alloy also reacted to completion under conditions of transient heating to temperatures in the range 600 to 700°C. However, the course of the self-sustained reaction of the titanium-containing alloy differed markedly from that of the molybdenum-containing alloys. A temperature-time curve for the titanium-containing alloy is shown in Figure IV-41, and the appearance of the completely oxidized residue is shown in Figure IV-39F. In Figure IV-41, it will be noted that the power was turned on again briefly during the experiment. This was done because it had been anticipated that reaction would sustain itself at temperatures of 600 to 660°C. Instead, Figure IV-41 shows that the titanium-containing specimens reacted in a sustained manner at a temperature of about 360°C as contrasted with 600 to 660°C for the molybdenum-containing specimens. The titanium-containing specimen required about 205 min to react completely. During the oxidation, the specimen swelled and eventually fell apart in platelets. No smoke was generated by the self-sustained oxidation of the titanium-containing alloy specimens.

c. RESULTS OF BURNING PROPAGATION EXPERIMENTS

Experiments designed to determine whether propagating combustion could be initiated were performed with the nominal 2 by 0.5 in. plates. The results (extents of reaction) are also given in Table IV-11 (column 6). Control experiments with stainless steel plates showed the nature of the temperature distribution induced within inert plates when they were heated only at the bottom end. Maximum temperatures near the top ends ranged from 175 to 306°C for initial maximum temperatures from 686 to 1064°C at the bottom ends. A control experiment with a 0.12-in. thick normal uranium plate showed that no propagation occurred and that the extent of reaction was only 1.3% throughout the heating-cooling cycle. Most of the reaction was limited to the lower, heated end of the specimen.

Propagation experiments performed with molybdenum-containing alloy specimens (Figure IV-42A) showed that, with one exception, no propagating reaction occurred. One 0.12-in. thick specimen, containing 25 w/o plutonium and 2.5 w/o molybdenum, began to react in a self-sustaining manner near the center of the specimen. The temperature at both ends of the specimen gradually reached about 600°C, as shown in Figure IV-43 and the entire sample reacted to completion (see Figure IV-42C). In all of the other propagation experiments, with a maximum bottom temperature of from 850 to 954°C, the temperature of the molybdenum-containing specimen decreased monotonically, and from 0.7 to 2.3% overall reaction oc-

U, 20 w/o Pu, 2.5 w/o Mo (0.5 by 0.5 by 0.2 in.)

A. Specimen before test

B. Result after nonsustained reaction (Specimen heated to 979°C; 5% reaction)

C. Result after a sustained reaction (Specimen heated to 655°C; 100% reaction)

U, 25 w/o Pu, 3 w/o Ti (0.5 by 0.5 by 0.2 in.)

D. Specimen before test

E. Result after nonsustained reaction (Specimen heated to 952°C; 6.2% reaction)

F. Result after a sustained reaction (Specimen heated to ~563°C; 100% reaction)

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FIG. IV-39. Uranium-Plutonium-Molybdenum and Uranium-Plutonium-Titanium Ternary Alloy Specimens Before and After Sustaining Reaction Experiments in Air.

curred. Typical temperature-time behavior during these experiments is shown in Figure IV-44. The appearance of a reacted nonpropagating sample is shown in Figure IV-42B, where it is apparent that reaction was concentrated at the lower (heated) end.

Propagation experiments with titanium-containing alloy specimens showed that no propagating reaction occurred. The overall extent of reaction ranged from

1.5–2.0% for 0.20-in. thick specimens to 8.4% for a 0.12-in. thick specimen (see Table IV-11).

d. EXPERIMENTS WITH PRE-OXIDIZED SPECIMENS

A final series of experiments was designed to determine if the oxide coating generated during a "high temperature" sustaining experiment would protect

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FIG. IV-40. Typical Temperature-Time Trace for a U, 20 w/o Pu, 2.5 w/o Mo Specimen (0.5 by 0.5 by 0.2 in.): Sustaining Reaction in Air.

108-9622 T-2

FIG. IV-41. Typical Temperature-Time Trace for a U, 25 w/o Pu, 3 w/o Ti Specimen (0.5 by 0.5 by 0.2 in.): Sustaining Reaction in Air.

A. Specimen before test.

B. Result after a nonpropagating reaction (Specimen heated to 980°C; 1.9% reaction)

C. Result after a propagating reaction (Specimen size was 2 by 0.5 by 0.12 in., heated to 931°C and 100% reaction).

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FIG. IV-42. U, 25 w/o Pu, 2.5 w/o Mo Specimens (2 by 0.5 by 0.2 in.) Before and After Propagation Reaction Experiments in Air.

specimens from the self-sustaining reaction induced during "low temperature" sustaining experiments. This series of experiments was performed with a 0.5 by 0.5 by 0.2 in. specimen of each of the three ternary alloy compositions.

The experiment with the SEFOR material (nominal composition: U, 20 w/o Pu, 2.5 w/o Mo) proceeded through several steps. First, the sample was heated to 957°C in 0.20 min at which time the power was turned off. The sample then cooled to room temperature without severe oxidation. The next day, the sample was heated to 752°C and the heating was terminated. The sample temperature then became steady at 638°C and it was apparent that the sustaining reaction had been initiated. The sustaining reaction was terminated by turning on the induction power for 0.16 min, thereby increasing the sample temperature to 990°C. The in-

duction power was then turned off and the sample cooled to 80°C. Turning on the induction power for another 0.16-min period raised the sample temperature to 825°C, thereby resulting in a self-sustaining reaction at about 600°C which continued to sample exhaustion.

A similar experiment was performed with an alloy plate having the nominal composition U, 25 w/o Pu, 2.5 w/o Mo. The sample was put through four heating-cooling cycles. Initial temperatures in the range 750 to 881°C resulted in a self-sustained reaction. Rapid heating to temperatures from 985 to 1000°C terminated the sustained oxidation reaction and resulted in cooling to room temperature within a few minutes.

An experiment with a sample having the nominal composition U, 25 w/o Pu, 3 w/o Ti followed a somewhat different course. The sample was heated to maxi-

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FIG. IV-43. Typical Temperature-Time Trace for a U, 25 w/o Pu, 2.5 w/o Mo Specimen (2 by 0.5 by 0.12 in.): Propagating Reaction in Air.

mum temperatures ranging from 612 to 835°C in 5 heating-cooling cycles without initiation of sustained reaction. A sixth cycle in which the sample reached a temperature of only 400°C also failed to induce a sustained reaction. One further cycle which brought the sample temperature to 515°C did result in a self-sustaining reaction at a steady temperature of about 370°C.

e. DISCUSSION

A probable explanation for the complex oxidation behavior of the ternary uranium-plutonium alloys can be developed from the results of more comprehensive studies with pure uranium and pure plutonium. Extensive isothermal studies of the oxidation of uranium⁵¹ and plutonium⁵² have been carried out at this laboratory. Results from the oxidation studies with pure uranium and two uranium-rich binary alloys showed

that pure uranium and a 1 a/o copper alloy have maxima in their oxidation rates owing to a transition from a low temperature reaction regime to a high temperature reaction regime in the region 400 to 500°C.⁵¹ Uranium containing 1 a/o aluminum did not undergo a transition in reaction rate. It was also shown that neither the high temperature nor the low temperature reaction rates were truly linear. At temperatures below 400°C, the reaction rate accelerated as oxidation proceeded at constant temperature. Above 500°C, the reaction rate decreased as oxidation proceeded, i.e., the oxide was somewhat protective. To a first approximation, however, the results with unalloyed uranium can be described in terms of two linear reaction regimes with a transition in the region 400 to 500°C. The nature of the transition is markedly influenced by alloying additions.

Pertinent results from the plutonium study show that unalloyed plutonium also undergoes a transition from a more rapid linear reaction to a less rapid linear reaction at about 400°C.⁵² (The plutonium oxidation is initially parabolic; however, the reaction rate becomes constant after only a slight oxide film is developed. For considerations involving sustained oxidations, then, plutonium can also be considered to follow a linear oxidation law.)

Isothermal oxidation rates are not available for the U-Pu-Mo and the U-Pu-Ti ternary alloys of interest. The results of the burning tests, however, indicate that the ternary alloys follow linear rate laws and probably also have maxima in the rates at the temperatures of self-sustained reaction, i.e., 600 to 660°C for the U-Pu-Mo alloys and 360 to 370°C for the U-Pu-Ti alloys. The linearity of the reaction rate during the self-sustained oxidations is evidenced by the fact that the temperature appeared to be very constant for long periods of time.

The observed behavior of the ternary alloys can be explained in terms of two linear reaction regimes characteristic of both unalloyed uranium and unalloyed plutonium. The results of the burning tests indicate that there is a hysteresis effect in the transition from one regime to another. This is diagrammed qualitatively in Figure IV-45. Curve "a" represents the reaction rate for the low temperature regime while curve "b" represents the reaction rate for the high temperature regime. The reaction rate variation with temperature is usually found to follow the Arrhenius law:

$$\log (\text{rate}) = \exp \left(-\frac{\Delta E}{RT} \right) \quad (51)$$

where ΔE = activation energy

R = gas constant

T = temperature.

⁵¹ L. Baker, Jr. and J. D. Bingle, *J. Nucl. Mater.* **20**, 11 (1966); see also ANL-6543, p. 175.

⁵² J. G. Schnizlein and D. F. Fischer, "The Kinetics of Oxidation of Plutonium Metal and a Plutonium-3.4 a/o Aluminum Alloy at Temperatures from 140 to 550°C", *J. Electrochem. Soc.*, **114**(1), 23-29 (January 1967).

108-9626 T-2

FIG. IV-44. Typical Temperature-Time Trace for a U, 25 w/o Pu, 2.5 w/o Mo Specimen (2 by 0.5 by 0.2 in.): No Propagating Reaction in Air.

Alloys. (Curve a: Reaction rate in low temperature regime. Curve b: Reaction rate in high temperature regime. Curve c: Reaction rate (or heat generation rate) required to maintain specimen at temperature. Arrow 1: Rising temperature transition. Arrow 2: Falling temperature transition.)

108-9621 T-2

FIG. IV-45. Diagram Indicating Proposed Mechanism of Self-Sustained Oxidation of U-Pu-Mo and U-Pu-Ti Ternary

The reaction rates (Figure IV-45) were therefore assumed to increase in an approximately exponential manner with increasing temperature. If the metal temperature is increased from room temperature, the reaction rate will follow curve "a" and the transition to the high temperature regime will proceed along arrow 1. Further increases in temperature will increase the reaction rate along curve "b". Cooling from high temperatures occurs along curve "b". The transition to the low temperature regime occurs at arrow 2.

The hysteresis behavior just described has been observed to occur with pure plutonium (ANL-6800, p. 362). In the experiments with pure plutonium, a sample was brought to 440°C and the reaction rate was determined (by means of a thermobalance apparatus) to be characteristic of the high temperature regime. The sample was then cooled and the linear reaction rate determined at each of a series of lower temperatures. The observed rate followed an extrapolation of the high tem-

temperature rate down to almost 300°C (100°C below the transition temperature observed at rising temperatures). At a temperature as low as 150°C, the observed rate was almost a factor of 10 lower than the normal rate. When the sample was cooled to room temperature overnight and then reheated, the higher reaction rate was again observed, suggesting that the sample could not be permanently passivated by controlled preoxidation.

One requirement for the development of a self-sustained reaction is that the rate of heat generation (proportional to reaction rate) is equal to or greater than the heat loss rate from the sample at the reaction temperature. This is represented by the shaded area in Figure IV-45 where the reaction rate exceeds the rate required to maintain the sample at the reaction temperature (curve "c"). The location of curve "c" on a plot such as that in Figure IV-45 evidently depends upon the specimen size and shape and the temperature of the environment. It could also be affected by air flow velocity and the reflectivity of the surroundings.

The foregoing discussion points out the fact that the occurrence of a self-sustained reaction is not a unique property of a metal but also depends upon the environment. Thus, if the sample is arranged in such a way as to increase the heat loss rate and, in effect, raise the level of curve "c" in Figure IV-45 so that there would be no intersection with curve "a-1-b", then there would be no self-sustained reaction. Locating the reactive metal sample partially within an inert cladding material would increase the heat-dissipating capability by decreasing the reactive surface area relative to the total surface area. It would be expected, therefore, that even partially clad alloy plates would not necessarily be subject to a sustaining reaction. On the other hand, arrangements which tend to conserve heat, i.e., lower the level of curve "c", would be expected to promote the tendency for a self-sustained reaction. The simultaneous heating of a large number of plates in close proximity would result in a decreased overall heat loss rate and increase the likelihood of sustained reaction.

Evidence for a maximum in the reaction rate of a U-Pu-Mo alloy was found in previous ignition experiments (ANL-6800, p. 378). A sharp increase in self-heating (reaction rate) between 600 and 700°C was observed for a U, 30 a/o Pu, 6 a/o Mo alloy. No ignition experiments were performed for ternary U-Pu-Ti alloys in those studies.

Some approximate values of reaction rates for the ternary alloys can be calculated from the thickness of the specimens and the overall consumption time. For example, the approximate reaction time for the U-Pu-

Mo alloy was 50 min, and during this period one-half the thickness of the plate, 0.25 cm, was reacted. The oxidation rate in terms of the oxygen consumed [assuming formation of (U,Pu)O₂] is:

$$\begin{aligned}\text{Rate} &= \frac{(17 \text{ g/cm}^3) (0.25 \text{ cm}) (32 \text{ g O}_2)}{(50 \text{ min}) (238 \text{ g U,Pu})} \\ &= \frac{0.011 \text{ g O}_2}{\text{cm}^2 \text{ min}}\end{aligned}$$

for U, 20–25 w/o Pu, 2.5 w/o Mo at 600°C. For the U-Pu-Ti alloy, the oxidation rate is:

$$\begin{aligned}\text{Rate} &= \frac{(17 \text{ g/cm}^3) (0.25 \text{ cm}) (32 \text{ g O}_2)}{(205 \text{ min}) (238 \text{ g U,Pu})} \\ &= \frac{0.003 \text{ g O}_2}{\text{cm}^2 \text{ min}}\end{aligned}$$

for U, 25 w/o Pu, 3 w/o Ti at 360°C.

The approximate reaction rate for the molybdenum-containing alloy, 11 mg O₂/(cm²)(min), may be compared with values of about 2 mg O₂/(cm²)(min) for both uranium (see Ref. 51) and plutonium (see Ref. 52) at 600°C. Similarly, the approximate reaction rate for the titanium-containing alloy, 3 mg O₂/(cm²)(min), may be compared with values of 0.4 mg O₂/(cm²)(min) for both uranium and plutonium at 360°C.

The chemical mechanisms of the oxidation reactions under study are only poorly understood. Although one might relate the maxima in the observed reaction rates to temperatures of metallic phase transitions, it is generally found that better correlations are obtained when phase transition temperatures of the oxide are considered. The rates of metal oxidation reactions are usually controlled by the rates of transport of either oxygen ions or metallic ions through a coherent layer of oxide near the metal-oxide interface. Thus, while pure plutonium metal exhibits five phase transitions between room temperature and the melting point, only two regimes of oxidation rate are observed.⁵² The change in the oxidation rate of pure plutonium was, therefore, associated with the development of a two-phase field in the plutonium-oxygen phase diagram. Similarly, the rate transition in the oxidation of pure uranium at 450°C is probably related to the increased oxygen solubility in UO₂ at temperatures above 450°C. The effects which added elements can have on oxidation kinetics are not understood because of the variety of ways in which added elements can affect ionic transport in solid oxides. Added elements can not only markedly change the electrical properties of oxide films, but also they can cause phase changes and gross structural changes, all of which can affect oxidation rates.

V

Energy Conversion¹

(A. D. Tevebaugh, J. D. Bingle)

A regenerative emf cell operates in a closed cycle to convert heat to electricity. The studies being undertaken at Argonne are concerned with devising regenerative cell systems which can be coupled eventually to a reactor heat source. The principal potential advantages of these systems are the elimination of most of the moving parts that are found in conventional systems, compactness, (a relatively low weight per unit of

power output), a long, maintenance-free life, and high temperature operation for those applications where heat rejection at high temperature is required. The applications of such systems might be for remote terrestrial and extraterrestrial power units, energy depots for armed services, and propulsion units for ships and large vehicles.

A. REGENERATIVE EMF CELLS—PHYSICAL-CHEMICAL LABORATORY STUDIES

Regenerative emf cell systems would operate continuously in a closed Carnot cycle, subject to Carnot efficiency limits for the overall conversion of heat to useful energy. An emf cell would function in one isothermal leg of a Carnot cycle; regeneration of the cell products could be accomplished either by thermally dissociating the products of the cell reaction or by operating a second cell in the high-temperature isothermal leg of the Carnot cycle. In the systems currently under investigation, the cell products have been decomposed into the cell reactants by spontaneous thermal regeneration. This type of regeneration requires the physical separation at high temperature of the anode and cathode reactants. These considerations have led to the study of two types of emf cells for possible application in a regenerative cycle. These are the hydride cell and the bimetallic concentration cells.

The hydride cell consists of an anode of molten metal, an electrolyte of molten salts containing the

anode metal ion, and a hydrogen gas cathode. In cell operation, the liquid anode metal is oxidized to ions of the metal and the hydrogen gas is reduced to hydride ions. At the present time, only lithium hydride is of practical interest for application in a regenerative hydride cell.

A bimetallic cell has two liquid metal electrodes in contact with an electrolyte which contains only salts of the anode metal. The metals currently under consideration are lithium and sodium for the anode and bismuth, tin, and lead for the cathode. The overall cell reaction is the oxidation of the anode metal to produce metal ions in the electrolyte, and reduction at the cathode of the metal ions to produce an alloy in the cathode.

Lack of basic data in the pertinent areas—thermodynamic, chemical, physical, kinetic, and solid state—handicaps the development of any regenerative emf cell system. The current program is involved in obtaining selected pieces of fundamental data in all areas except solid state electrolyte phenomena.

¹ A summary of this section is given on pages 18 to 19.

1. Bimetallic Cell Systems: Sodium-Bismuth Cell Studies (M. S. FOSTER, G. H. McCLOUD)

Studies of the thermodynamic properties of sodium-bismuth alloys have been made using cells of Type 1:

and of Type 2:

In preliminary studies of cells of Type 2, it was observed that the nonelectrochemical (or irreversible) transfer of sodium from the anode, through the electrolyte, and into the cathode was sufficiently large to cause a steadily decreasing cell potential as the concentration of sodium in the cathode alloy increased. Therefore, a cell of Type 2 could be operated only at a single temperature during a run. For calculations of thermodynamic properties, the initial potential of the cell is required. This potential is obtained by extrapolation to zero time. In order to obtain data at more than one temperature per experiment, cells of Type 1 have been operated.

The electromotive forces of cells of Type 1 have been measured previously (see ANL-7125, p. 211), using cathode alloy compositions of 10, 20, 30, 40, and 50 a/o sodium ($X_{\text{Na}} = 0.10, 0.20, 0.30, 0.40, \text{ and } 0.50$). A cell with a cathode composition of 60 a/o Na-Bi has now been run. It has also been shown that the previously reported results for the cell with the cathode alloy composition of 50 a/o sodium were biased by a loss of potential due to an insufficiently high off-balance input impedance (10^6 ohms) of the potentiometric recorder used. The current drawn was sufficient to polarize the cell. In other experiments in this series, a potentiometric electrometer with an input impedance of 10^{13} ohms was used to correct this problem. The voltages now observed for the cell with cathode composition of 50 a/o sodium are ~ 10 to 15 mv higher than those previously reported, whereas the curves for $X_{\text{Na}} = 0.10, 0.20, 0.30, \text{ and } 0.40$ were unaffected by the change in input impedance.

All of the data obtained to date are shown in Figure V-1. The discontinuities in the slopes of the lines for $X_{\text{Na}} = 0.30$ and 0.40 are each taken to indicate the transition from a single liquid phase system (at temperatures above the break) to a two-phase system consisting of a liquid and NaBi(s) at lower temperatures (see ANL-7125, p. 211). These breaks were found to be $\sim 10^\circ\text{K}$ higher than those seen in the phase diagram listed by Hansen and Anderko.²

² M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 322.

In Figure V-1, a slight break can also be noted for the cell with a cathode composition of $X_{\text{Na}} = 0.60$. According to Hansen and Anderko, for this composition and at temperatures below 948°K , a two-phase equilibrium exists between $\text{Na}_3\text{Bi(s)}$ and a liquid alloy whose composition varies with temperature. As can be seen in the figure, the break does not result in a sufficient difference in slopes so as to indicate the exact temperature of the break.

The data for the cell with a cathode composition of $X_{\text{Na}} = 0.50$ should exhibit a discontinuity in slope at 793°K , according to Hansen and Anderko. However, no indication of such a change of slope can be seen in Figure V-1, even though cells were operated at temperatures below 793°K . The extrapolation of the data from the cells with 60 and 50 a/o sodium cathode alloys indicates that the intersection occurs near 748°K , or some 45 degrees lower than the published phase diagram indicates. This suggests that the phase diagram should be reinvestigated, especially in this composition range.

The differences in voltage between cells with solid

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FIG. V-1. Potential-Temperature-Composition Characteristics of the Cell Na/NaCl(s)/Na-Bi ($X_{\text{Na}} = \text{a/o Na}$).

electrolytes (Type 1) and cells with liquid electrolytes (Type 2) have previously been reported (ANL-7125, p. 212) as being ≤ 15 –20 mv, with cells of Type 2 showing the higher values. This difference is thought to be due to the problem of electronic conduction. Before a complete analysis of the data from both types of cells can be made, the importance of electronic (as opposed to ionic) conduction in both solid and liquid electrolytes must be evaluated. To establish the magnitude of the electronic conduction, studies were conducted of the Faradaic efficiency (number of equivalents of sodium deposited per Faraday passed through the external circuit).

Two experiments (one at 841°K and the other at 886°K) on the electrodeposition of sodium were made using cells in which the liquid electrolyte, a eutectic mixture of NaI, NaCl, and NaF, was saturated with sodium metal. In these experiments, sodium metal (initially contained in an inverted tantalum cup) was electrochemically transferred through the electrolyte to a tantalum flag suspended inside an alumina tube, which served as a cathode. A total of 1800 coulombs (2 amp for 900 sec) was passed through the external circuit. A sample consisting of the metallic sodium at the cathode and the immediately surrounding electrolyte was dissolved in water. This solution was titrated with standard acid, and the result was used to calculate the total metallic sodium content of the sample. A sample of the remaining electrolyte was also taken immediately after the electrolytic deposit of sodium was removed. This sample was analyzed for metallic sodium in the same manner, and the result was used to correct for the dissolved sodium in the electrolyte that had been removed with the electrodeposited metal.

At 841°K, the observed Faradaic efficiency was 90.4%; at 886°K, the observed efficiency dropped to 82.5%. It is reasonable that the efficiency be lower at the higher temperature, owing to the increased solubility of sodium in the electrolyte at higher temperatures.

The effects of both ionic and electronic conductivity in a liquid electrolyte have been discussed previously (ANL-7125, p. 231). In that report it was demonstrated that for a cell which is operated under steady-state conditions, the observed open-circuit voltage will be less than the true thermodynamic open-circuit potential by an amount

$$-\Delta E^o = \frac{R_g T}{F_1} \ln \left(\frac{\kappa_i + \kappa_e^A}{\kappa_i + \kappa_e^C} \right) \quad (1)$$

where κ_i is the metal anode ion conductivity of the electrolyte; κ_e^A , the electronic conductivity in the anolyte; κ_e^C , the electronic conductivity in the catholyte; R_g , the gas constant; T , the absolute temperature; and F_1 , the value of the Faraday. If the assumption is made that $\kappa_e^C \ll \kappa_e^A$ (on the basis that the concentration of metal in the catholyte is much less than in the anolyte), then we may write

$$-\Delta E^o = \frac{R_g T}{F_1} \ln \left(\frac{\kappa_i + \kappa_e^A}{\kappa_i} \right) = \frac{R_g T}{F_1} \ln \left(\frac{1}{\eta} \right)$$

where η is the Faradaic efficiency as determined in a melt saturated with anode metal. For a concentration cell having sodium as the anode metal and operating under steady-state conditions, the experimentally observed Faradaic efficiencies indicate that the voltage losses due to cell current flow and irreversible transfer will be 7 and 15 mv at 841 and 886°K, respectively.

2. Lithium Hydride Cell Studies: Conductivity of Lithium Hydride-Lithium Halide Electrolytes (C. E. JOHNSON, E. J. HATHAWAY, N. P. QUATTROPANI)

The search for an electrolyte suitable for use in a lithium hydride emf cell has fostered investigations of the lithium hydride-lithium halide (Cl^- , Br^- , I^-) binary fused salt systems. Temperature-composition data obtained for these systems showed that each has a simple eutectic (see ANL-7125, p. 203). Using the solid-liquid equilibrium temperature data, calculations were made of the excess chemical potential for each component of the binary system. These calculations indicate that all systems show positive deviations from ideality for the lithium hydride component of the electrolyte. These positive deviations can be totally accounted for by assuming that the system is made up of dimeric lithium halide (Li_2X_2) species and lithium

hydride monomer.³ Indications of dimeric lithium halide species have also been obtained from interpretations of the freezing point depression of lithium hydride by the lithium halides.³ If such associated species are present in the electrolyte, a significant change in the normal ionic character of the electrolyte might result. In an attempt to elucidate further the nature of the species in these fused salt solutions, electrical conductance measurements are being made.

In order to measure the electrical conductance ($1/R$) of fused salt solutions, one must first select the method to be used and then the materials of construction for

³ C. E. Johnson, S. E. Wood, and C. E. Crouthamel, *J. Chem. Phys.* **44**, 884 (1966).

the electrodes. Lithium hydride acts much the same as lithium metal in being highly corrosive towards most materials except molybdenum, tungsten, niobium, and types 316 and 347 stainless steels.

After the initial studies, it was concluded that the conductivity cell developed by Bronstein and co-workers⁴ gave greatest promise of success. This conductivity apparatus employs two rigidly mounted parallel molybdenum electrodes immersed in the melt contained in a molybdenum cup. The depth of immersion of the parallel electrodes is accurately measured by means of a micrometer screw that is directly attached to the electrodes.

The resistance of a homogeneous solution, measured by immersing two parallel electrodes into the salt, is a linear function of the depth of immersion. The difference in conductance per unit depth is a constant or

$$(1/R_2 - 1/R_1)/(d_2 - d_1) = S, \text{ ohm}^{-1} \text{ cm}^{-1} \quad (2)$$

where R_1 and R_2 are resistances at depths d_1 and d_2 , respectively. R_1 and R_2 are obtained by subtracting from the total resistance both the resistance of the electrodes above the solution and one-half the resistance of the electrodes immersed in the solution. For any metal electrode of uniform cross section and uniform but small potential drop along the immersed length as compared with the potential drop in the melt, the ef-

fective resistance can be taken to be one-half the resistance that this length of the electrode would have when not immersed. In this consideration, the area of the bottom of the electrode is negligible compared to the total immersed area. The resistance of the molybdenum electrodes was measured at the temperatures of the experiments by shorting them at various lengths with a copper bar clamp.

Fused salts have very low resistivities; for example, the resistivity of LiCl at 650°C is 0.169 (ohm) (cm), whereas that of the best conducting aqueous system is >1 (ohm) (cm). Thus a very sensitive bridge is needed for accurate measurement of the electrolyte resistance. Such a transformer bridge, built by J. Bobis of the Electronics Division, has been incorporated into the apparatus.

The cell constant, C , defined as conductivity/ S , for this parallel electrode assembly has been determined by measuring the electrical conductivity of solutions of cadmium in CdCl₂ (i.e., by using these solutions as standards). The conductivity of these solutions was first determined by Aten⁵ and recently checked by Bronstein et al.⁴ For this particular parallel electrode assembly, a cell constant of 0.633 was determined. Measurements are now being made of the conductivities of the lithium hydride-lithium halide binary mixtures.

3. Liquid-Vapor Equilibria of Intermetallic Systems (A. K. FISCHER, S. A. JOHNSON)

Knowledge of the temperature-pressure-composition relationships in the pertinent liquid-vapor equilibria is necessary for the design of the regenerator of a bi-metallic concentration cell. Complementary techniques are being used (see ANL-7125, pp. 221–223) to provide the total vapor pressure and vapor composition measurements which delineate these relationships. The total pressure determinations have been made by the quasi-static (Rodebush-Dixon)⁶ technique; data have been obtained for selected liquid compositions over a range of temperature. The vapor composition and vapor density measurements have been made by the transpiration (carrier gas) technique (ANL-7055, p. 222); selected liquid compositions have been studied at a fixed temperature. At the present time, measurements have been completed for the sodium-bismuth system and are in progress for the sodium-lead system.

a. SODIUM-LEAD SYSTEM

Total vapor pressure measurements have been made for sodium-lead mixtures containing 50 and 70 a/o lead. The temperature range covered was 685 to 867°C for the former concentration, and 785 to 888°C for the latter. These data are presented in Figures V-2 and V-3.

Exploratory transpiration experiments were carried out on the sodium-lead liquid phases for compositions of 70, 80, and 90 a/o lead. The temperature at which these measurements were made was 850°C, a plausible regeneration temperature for the sodium-lead cell. The partial pressures of monatomic sodium were 15.2, 6.7, and 1.7 torr for liquid compositions of 70, 80, and 90 a/o lead, respectively. The composition of the vapor over the 70 and 80 a/o lead liquids was about 98.5 a/o sodium.

The vapor density (transpiration) data, together with equilibrium constants for the gaseous sodium monomer-dimer reaction, permit calculation of the activity of sodium in the melt. Since lead is monatomic

⁴ H. R. Bronstein, A. S. Dworkin, and M. A. Bredig, *J. Phys. Chem.* **66**, 44 (1962).

⁵ A. H. W. Aten, *Z. physik Chem.* **73**, 578 (1910).

⁶ W. H. Rodebush and A. L. Dixon, *Phys. Rev.* **26**, 851 (1925).

in the vapor phase, the density data can be used without additional gaseous equilibrium data to calculate the activity of lead in the liquid phase. Using known values for the equilibrium constant for the reaction

and allowing for the small amount of lead in the vapor, the partial pressure of monatomic sodium can be cal-

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FIG. V-2. Total Vapor Pressure for the System 50 a/o Na-50 a/o Pb as Measured by Quasi-Static Method.

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FIG. V-3. Total Vapor Pressure of System 70 a/o Pb-30 a/o Na as Measured by Quasi-Static Method.

TABLE V-1. EMF OF THE CELL, Na/ELECTROLYTE/Na-Pb, AS A FUNCTION OF TEMPERATURE AND CATHODE COMPOSITION

Cathode Composition (a/o Pb)	Cell Emf (volt) at Indicated Temperature	
	850°C ^a	425°C ^b
70	0.323	0.335
50	0.163	0.195

^a Calculated from activity data.

^b Calculated from data of Hultgren.⁷

TABLE V-2. PARTIAL MOLAR FREE ENERGY OF SODIUM IN SODIUM-BISMUTH MELTS

Composition (a/o Na)	Coefficients for $\Delta\bar{F}_{\text{Na}} = A + BT + CT^2$			Temperature Range of Measurements (°K)
	A	B	C	
90	1539.5	-2.454	-0.000763	892-1114
80	10338.0	-17.053	-0.006434	1076-1181 ^a
77.5	3991.7	-5.896	0.001143	1101-1179 ^a
75	-13476.0	9.874	-0.001714	1116-1228 ^a
60	-2157.4	-14.96	0.00834	1118-1242

^a The curves should not be extrapolated to temperatures lower than 1070, 1093, and 1115°K for the compositions 80, 77.5, and 75 a/o sodium, respectively. At lower temperatures than these, the liquid-vapor loop intersects the liquid-solid region of the phase diagram (see ANL-7125, p. 223).

culated from the total vapor pressure data, and, thence, the activity of sodium in the liquid phase may be derived.

The activity calculated by these methods from data for the 50 and 70 a/o Pb systems was converted to an emf which is the emf that the corresponding sodium-lead cell would exhibit at the regeneration temperature. The results are compared in Table V-1 with emf's derived from low temperature data of Hultgren.⁷ It can be seen that, for a given composition, the emf's at the two temperatures are very close. This indicates that there is no appreciable aid to regeneration in the form of a favorable change in free energy as the temperature is raised.

b. SODIUM-BISMUTH SYSTEM

The total vapor pressure data for sodium-bismuth systems containing 90, 80, 77.5, 75, and 60 a/o sodium (see ANL-7125, p. 223) were used, together with the appropriate equilibrium constants, to calculate the activities of sodium in the respective melts at a series of temperatures. A second degree polynomial w:

⁷ R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, *Selected Values of Thermodynamic Properties of Metals and Alloys*, John Wiley & Sons, Inc., New York, 1963.

fitted by the method of least squares to the resulting set of activity data for each composition. The expressions for the partial molar free energy of sodium are

tabulated in Table V-2. Further treatment of the data to yield entropy and enthalpy information will be made.

4. Laser-Excited Raman Spectrophotometry of Fused Salts (E. L. GASNER)

A better understanding of the structure of molten salts may be gained from the identification of species and molecular association (for example, complex ions, neutral molecules, pseudo-lattice structures) in these systems. For this purpose, a laser-excited Raman spectrophotometer has been designed and constructed and is presently being tested. Initial experimental work will involve a search for spectra of Raman-active species which may be present in solutions of intermetallic compounds (such as Li_3Bi) in molten alkali halide solvents.

A brief description of the major components of the apparatus follows. The source of excitation light is a Spectra Physics Model 125 continuous He-Ne gas laser with a nominal power output of 50 mw at 6328 Å. The dispersive unit is an f/6.8 Spex Model 1400 scanning double monochromator equipped with a pair of 103-mm square, 1200 lines/mm gratings blazed for

7500 Å. The photomultiplier tube is an R136 from the Hamamatsu Television Co., Ltd. The signal from the photomultiplier can be amplified either by means of a DC amplifier or, after chopping the laser beam with a conventional rotating sector disc, by means of a lock-in AC amplifier. The amplified signal is fed to a strip chart recorder.

Prior to its use in the study of fused salt solutions, the apparatus was tested by obtaining the spectra of liquid carbon tetrachloride and of gaseous oxygen and comparing them with the same spectra obtained using conventional Raman spectrophotometers. These preliminary experiments were performed with a low-power (~ 1 mw at 6328 Å) Perkin-Elmer Model 5200 He-Ne laser.

A practical method for photoelectric recording of Raman spectra of gases was first reported by Yoshino

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FIG. V-4. The 459 cm^{-1} Raman Band of CCl_4 . (Excitation source, 1-mw 6328 Å He-Ne laser. Scan, 0.52 $\text{cm}^{-1}/\text{min}$; spectral bandpass, 1.25 cm^{-1} ; time constant = $RC = 30$ sec.)

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FIG. V-5. The Pure Rotational Raman Spectrum of O_2 at One Atm Pressure. (Excitation source, 1-mw 6328 Å He-Ne laser. Scan, $10\text{ cm}^{-1}/\text{min}$; spectral bandpass, 2.5 cm^{-1} ; time constant = $RC = 10\text{ sec}$.)

and Bernstein,⁸ who used Toronto mercury arcs as the source of excitation light. The use of a He-Ne gas laser as a light source for obtaining Raman spectra of gases was recently reported by Weber and Porto.⁹ In their experiments, the sample was placed inside the laser cavity, and the spectra were recorded photographically. In this laboratory, the pure rotational Raman spectrum of oxygen gas was photoelectrically recorded with the sample cell placed outside the resonant cavity of the He-Ne laser.

The experimental results on the Raman spectra of liquid CCl_4 and gaseous O_2 are given in Figures V-4 and V-5. Both spectra were recorded in the first order. The signal from the photomultiplier was amplified with a DC amplifier. Values of slit widths, time constants, and scanning speeds are given in the legends. Each sample was contained in a Perkin-Elmer Model 211-0537 multiple reflection cell while the spectrum was being recorded.

The curve for CCl_4 , Figure V-4, gives an indication

of the overall sensitivity and resolution of the experimental apparatus. Use of the multiple reflection sample cell for recording the 459 cm^{-1} CCl_4 band gave about 25 times as much intensity as with a single pass of the 1-mw laser beam through a simple 10 mm by 10 mm by 35 mm absorption cell. The effective power was therefore equivalent to that of a single pass of a 25-mw laser beam. The isotopic fine structure is well resolved and, with a 30-sec time constant (where the time constant = RC), the signal-to-noise ratio is very high. This curve compares favorably with the results obtained by Brandmuller and Moser,¹⁰ who used a mercury arc excitation source, and with the earlier results obtained by Koningstein and Smith¹¹ who used a 6328 Å He-Ne laser excitation source.

The oxygen spectrum in Figure V-5 was obtained with an amplification about four times as great and a spectral bandpass two times as great as those used for the CCl_4 trace. The rotational lines are seen to be well resolved with a signal-to-noise ratio of about 8

⁸ T. Yoshino and H. J. Bernstein, *J. Mol. Spectry*, **2**, 213 (1958).

⁹ A. Weber and S. P. S. Porto, *J. Opt. Soc. Am.*, **55**, 1033 (1965).

¹⁰ J. Brandmuller and H. Moser, *Einführung in die Ramanspektroskopie*, Dr. Dietrich Steinkopf, Darmstadt, 1962, p. 406.

¹¹ J. A. Koningstein and R. G. Smith, *J. Opt. Soc. Am.*, **54**, 1061 (1964).

to 1. The signal-to-noise ratio is less than that obtained by Yoshino and Bernstein⁸ but the baseline is almost flat to within $\sim 15 \text{ cm}^{-1}$ from the exciting line. No grating ghosts were observed when the sample cell was filled with a monatomic gas, but some additional lines of the helium spectrum produced by the laser were observed. The use of a narrow bandpass optical filter and improved masking of the laser beam is planned to reduce the intensity of these lines. The multiple reflection cell increases the production of Raman

light by causing the laser beam to make a large number of passes through the sample. By adding mirrors of the type used by Yoshino and Bernstein,⁸ one should be able to increase the efficiency of collection of the Raman light which has been produced. However, the most promising source of improvement of signal-to-noise ratio lies in the use of a more powerful laser source. (Indeed, an argon laser is being used to obtain the rotational Raman spectra of simple gases, according to a recent report by Porto et al.¹²)

B. REGENERATIVE EMF CELLS—ENGINEERING STUDIES

Engineering studies have continued with the purpose of investigating the feasibility of developing a practical thermally regenerative emf cell, which would ultimately be coupled to a nuclear reactor, isotope unit, or

other heat source. Both bimetallic and hydride cells are being studied; however, during this reporting period, most of the engineering work has involved sodium-lead and sodium-bismuth bimetallic systems.

1. Experimental Bimetallic Cells (J. HESSON, H. SHIMOTAKE, G. ROGERS)

a. SODIUM-BISMUTH CELL

An experimental sodium-bismuth cell without a thermal regenerator was built and placed in operation on December 9, 1964 (see ANL-7055, p. 226) and was kept in operation at cell temperatures ranging from 535 to 650°C, with an average temperature of 550°C, for 17 months. At this time the cell operation was terminated owing to accidental shorting of heater transformers. The average open circuit voltage is 0.66 volt with a 30 a/o sodium-bismuth alloy as the cathode; however, with pure bismuth cathode metal, an open circuit voltage of 1.22 volts is obtained. The cell was discharged and then recharged electrically about every two days during the 17-month period. The frozen electrolyte-silicone rubber insulator-pressure seal which was incorporated with the stainless steel flange of the cell body showed no sign of deterioration.

b. SODIUM-LEAD CELL

Operation of the experimental sodium-lead cell apparatus with attached thermally operated regenerator, described in ANL-7125, p. 228, has been continued. The cell and regenerator (see Figure V-6) are made of stainless steel and the cell has a frozen electrolyte-silicone rubber pressure seal. Sodium is regenerated from the sodium-lead cathode alloy by distillation. To

date, approximately 100 hr of operating time have been accumulated.

At the end of 36 hr of operation (9 runs), the cell was disassembled and a screen was installed in the anode (sodium) section of the cell to improve electrical contact of the sodium with the anode section of the cell body. In addition to improving the electrical contact, the screen enabled the system to be operated at a lower pressure. Previously (see ANL-7125, p. 228), it was necessary to operate the regenerator at 850°C and 7 mm Hg pressure and at 825°C and 6 mm Hg pressure to obtain currents of 5 and 2.5 amp, respectively, from the cell. After installation of the screen, these currents could be obtained at regenerator temperatures of 800°C and 3.5 mm Hg pressure and 780°C and 2.5 mm Hg pressure, respectively. A cell current of 2.5 amp at 0.28 volt was achieved at a cell temperature of 50°C and a regenerator temperature of 780°C. The output of current is limited by the sodium regeneration rate, which is in turn limited by various factors such as the regenerator temperature, evaporating area, the sodium concentration in the cathode alloys, and impurities in the cathode alloys.

¹² S. P. S. Porto, L. E. Cheesman, A. Weber, and J. J. Barrett, 50th Anniversary Meeting, Optical Society of America, March, 1966.

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FIG. V-6. Sodium-Lead Thermally Regenerative Emf Cell System.

2. Engineering Material Corrosion Studies (H. SHIMOTAKE, G. ROGERS, M. SILVERMAN)

Potential container materials for thermally regenerative bimetallic emf cell systems are being examined. In these systems, the operating temperature of the cell would be about 550°C , while that of the regenerator would be above 800°C for sodium-lead or sodium-tin and above 1000°C for sodium-bismuth or lithium-tin. The most serious type of corrosion encountered is dynamic corrosion, that is, the transport of container material from the hot zone of the system to the cold zone where precipitation may occur.

Although a considerable amount of information is available on alkali metal corrosion from work related to space and nuclear reactor projects, very little information has been found on corrosion by heavy metals at temperatures above 800°C . For these reasons, the cor-

rosion of proposed container materials by liquid cathode metals at temperatures near 1000°C is being studied. Both static and dynamic tests are being conducted.

a. STATIC CORROSION TESTS

For static tests, the materials under study were usually cut from sheet stock in the form of coupons, 1 by $\frac{1}{2}$ by $\frac{1}{8}$ in. The coupons and the liquid metal (bismuth, tin, or lead) were placed within a crucible fabricated from molybdenum-30 w/o tungsten, an alloy which is considered to be nearly inert to attack by bismuth, tin, or lead. The loaded crucible was placed in a stainless steel bomb located in a resistance-heated furnace and held at the test temperature (600

TABLE V-3. STATIC CORROSION OF VARIOUS MATERIALS BY BISMUTH, TIN, AND LEAD

Test Material	Bismuth			Tin			Lead		
	Temp. (°C)	Time (hr)	Results	Temp. (°C)	Time (hr)	Results	Temp. (°C)	Time (hr)	Results
<i>Refractory Metals</i>									
Molybdenum	1000	97	No corrosion. Wetted.	1000	26	Penetration, <15 μ depth.	—	—	—
				1000	97	Intergranular. Completely wetted.			
Niobium	1000	64	Dissolution, 30 μ thickness. Intergranular, <50 μ . Wetted.	1000	24	Slight dissolution. Intermetallic with dendrites, <20 μ thickness.	1000	94.5	Became brittle. Completely wetted.
	1000	137	Severe intergranular attack. Specimen became brittle.	1000	96	Severely attacked. Became brittle.			
Tantalum	1000	95	No apparent attack. Wetted.	1000	96	Penetration, <20 μ depth.	1000	100	No corrosion. Completely wetted.
Tungsten	1000	24	No apparent attack. No wetting.	1000	96	Penetration, <5 μ . Completely wetted.			
	1000	92	No corrosion. Slightly wetted.				1000	96	No corrosion. Partly wetted.
Mo-30 w/o W	1000	97	No corrosion.	1000	67	No corrosion. Slightly wetted.			
	1000	150	No corrosion. Wetted.				1000	135	No corrosion.
	~1000	>2300	No visible attack. Intermetallic, ~100 μ thickness.	~1000	>1200	No visible deterioration. Intermetallic, ~100 μ thickness.			
Mo-50 w/o Re	1000	91	No apparent attack. Intermetallic, <12 μ . Wetted.	1000	63.5	No apparent attack. Wetted.	—	—	—
Nb-1 w/o Zr	1000	167	Severe intergranular attack, <250 μ depth. Specimen became brittle.	1000	160	Intergranular attack, <100 μ depth. Completely wetted.	—	—	—
Nb-10 w/o W-2.5 w/o Zr	1000	71.5	Slight dissolution and pittings.	1000	87.5	Slight dissolution and pittings. Completely wetted.	—	—	—
Nb-28 w/o Ta-10 w/o W-1 w/o Zr	1000	137	Completely wetted. Became brittle.	1000	97.5	Wetted. Intermetallic, ~100 μ thickness.	1000	99	No corrosion. Wetted.
<i>Nonrefractory Metals</i>									
Armco iron	850	24	Slight attack.	a	—	—	—	—	—
	1000	50	Complete dissolution.						
1040 steel	1000	22	Intermetallic layer, <80 μ thick. Cr preferentially segregated.	a	—	—	—	—	—
304 stainless steel	850	97	Intergranular, <100 μ depth. No attacks found in vapor phase.	a	—	—	—	—	—
316 stainless steel	700	97	Slight dissolution. Decarburization, <5 μ depth in both liquid and vapor phases.	a	—	—	850	112	Slight dissolution. Wetted.
2 $\frac{1}{4}$ w/o Cr-1 w/o Mo steel	850	100	Slight dissolution, <14 μ . Very little wetting.	a	—	—	1000	100	Wetted. Dissolution, 300 μ thickness.
	1000	163	Intergranular, <200 μ . Completely wetted.						
Co-20 w/o Cr-15 w/o W-10 w/o Ni-3 w/o Fe	—	—	—	—	—	—	850	142	Slightly wetted. No corrosion.
							1000	119	Very slight attack. 50% surface wetted.
405 stainless steel	850	94.5	Slightly wetted. Intergranular, <40 μ thickness.	a	—	—	850	99	No attack. 40% surface wetted.

Continued

TABLE V-3—Continued

Test Material	Bismuth			Tin			Lead		
	Temp. (°C)	Time (hr)	Results	Temp. (°C)	Time (hr)	Results	Temp. (°C)	Time (hr)	Results
440 stainless steel	850	100.5	Wetted. Intergranular, <150 μ thickness.	^a	—	—	850	100.5	No corrosion. Completely wetted.
<i>Insulation Materials</i> High-purity alumina	600	99	No attack. No wetting.	600	77.5	No attack. No wetting.	—	—	—
	850	52	Partly wetted and grayed.	850	29	Slightly wetted.	—	—	—
	1000	72	Partly wetted and grayed, not electrically conducting.	1000	74	Completely wetted. Slightly conducting.	—	—	—

^a In view of the high solubility of this material in tin, no test was made.

to 1000°C) for a predetermined period of time. A summary of all test results, including those previously reported, is presented in Table V-3. Common materials including low carbon steel, pure iron, and stainless steels showed some degree of resistance in liquid bismuth and lead at the temperatures above 800°C. These materials were, however, not tested in liquid tin because of their high solubility in tin.

In the course of the study it has become apparent

that, although steel or stainless steel may be suitable for the cell portion of sodium-lead and sodium-bismuth systems, the only promising container materials for sodium-bismuth regenerators or sodium-tin cells and regenerators are the refractory metals and their alloys. (An exception is niobium and its alloys, which became brittle after exposure to either bismuth or tin at 1000°C.) Table V-3 illustrates the resistance to attack of several of these refractory metals.

TABLE V-4. DYNAMIC CORROSION OF VARIOUS MATERIALS BY BISMUTH, LEAD, AND SODIUM-BISMUTH AND SODIUM-LEAD ALLOYS

Loop Number	Test Material	Liquid Metal	Max Hot Leg Temp (°C)	Min Cold Leg Temp (°C)	Time (hr)	Results
2	1020 steel	Bi	550	450	1000	Dissolution, up to 250 μ depth.
3	1020 steel	Bi	800	700	24	Slight dissolution. Plugs formed, stopping circulation.
4	1020 steel	Bi	850	450	430	Leak developed. ^a Dissolution of up to 60% of the loop metal at the hot leg.
5	1020 steel	Bi	850	450	279	Leak developed. ^a Dissolution of up to 50% of the loop metal at the hot leg. Slight intergranular penetration.
6	1020 steel	Bi-20 a/o Na	850	450	125	Leak developed. ^a Dissolution of up to 50% of the loop metal at the hot leg.
9	1020 steel	Bi-30 a/o Na	650	550	1506 ^b	Slight mass transfer.
12	1020 steel	Pb	850	650	690 ^b	Plugs formed, stopping circulation.
17	1020 steel	Pb-30 a/o Na	800	600	345 ^b	Plugs formed, stopping circulation.
7	316 stainless steel	Bi	850	450	300	Leak developed. ^a Extensive mass transfer. Intergranular penetration.
8	316 stainless steel	Bi-25 a/o Na	650	550	4426 ^b	Dissolution of up to 65% of the loop metal at the hot leg.
11	316 stainless steel	Pb	850	650	706 ^b	Plugs formed, stopping circulation.
13	316 stainless steel	Pb-30 a/o Na	850	650	1224 ^b	Plus formed, stopping circulation.
15	316 stainless steel	Pb-30 a/o Na	800	550	348 ^b	Plugs formed, stopping circulation.
10	Mo-30 w/o W	Bi	1050	700	2488	Welding fractures developed in loop; no corrosion.
16	Tantalum	Pb-30 a/o Na	1050	750	932	Leak developed in stainless steel sheath.

^a The leak developed at the entrance section of the hot leg.

^b No leaks were found at the termination of experiment.

5. DYNAMIC CORROSION TESTS

Dynamic corrosion tests being conducted by means of loops fabricated of the test materials have continued. In these tests, the liquid metals are circulated in the loops by thermal convection. The loops are constructed of $\frac{1}{4}$ -in. pipe (0.54-in. OD and 0.364-in. ID) in the form of parallelograms about 10 in. high and 6 in. wide. Electric resistance heaters are used to maintain the four legs or sections of the loop at different predetermined temperatures. A description of the loops and their operation may be found in ANL-6925, p. 246 and ANL-7125, p. 235.

The results of all dynamic corrosion tests conducted to date are summarized in Table V-4. The results of the most recent dynamic corrosion tests confirmed earlier indications (see ANL-7125, pp. 234–236) that neither stainless steel nor low carbon steel is suitable for use in a sodium-bismuth cell system at temperatures above 800°C when the temperature difference between the hot and cold legs is more than 250°C.

In view of this severe dynamic corrosion, testing of refractory metal loops was initiated. Loop 10 was fab-

ricated of molybdenum-30 w/o tungsten. Because of the known welding difficulties with this material, very careful steps were taken during its fabrication. This loop was charged with bismuth and operated in an argon gas enclosure with cold and hot leg temperatures of 700–900 and 1050°C, respectively; after 2488 hr, a leak developed. Upon examination, linear fractures were found along the longitudinal axis of the loop pipe. However, metallographic examination showed no sign of corrosion by the liquid bismuth. The cause of the fractures was considered to be the result of the lack of annealing after welding.

Another loop, Loop 16, was constructed of type 316 stainless steel pipe lined with tantalum. This loop was charged with 30 a/o sodium-lead alloy and was operated with a hot leg temperature of 1050°C and a cold leg temperature of 750°C for 932 hr at which time a leak developed in the small joint section of the loop. This area was in the low temperature portion of the system, but was not protected by the tantalum lining and thus the 316 stainless steel pipe had been exposed to the liquid metal.

VI

Nuclear Constants¹

(D. C. Stupegia, A. D. Tevebaugh, J. D. Bingle)

The fast neutron program is directed toward the study of neutron cross sections that are useful in calculations of the breeding gain of fast reactors, and toward the use of the data to test theories of nuclear reactions. Of particular importance are (1) capture cross sections of structural and control materials; (2)

capture and fission cross sections of fissile and fertile species; and (3) neutron inelastic scattering cross sections. In the present program, several of the above types of reactions are under investigation. Current progress is reported below.

A. RADIATIVE CAPTURE (D. C. STUPEGIA, C. R. KEEDY, M. SCHMIDT, A. A. MADSON)

Radiative neutron capture cross sections are being measured as a function of neutron energies between a few keV and about 3 MeV. Since neutrons are absorbed unproductively in radiative neutron capture, the cross section data are needed in order to evaluate materials proposed for use in reactor structure and control.

The experimental technique is the activation method in which a sample is irradiated in a monoenergetic neutron beam and counted with a beta or gamma-ray counter. The monoenergetic neutrons are produced by bombarding lithium or tritium targets with protons from the Van de Graaff accelerator. The neutron intensity is measured with a fission chamber which counts fissions in a thin deposit of ²³⁵U.

The data are compared with calculations based upon the statistical model of the compound nucleus, which gives the energy averages of resonant compound nuclear cross sections. The calculations take into account the variation of radiation width and level density with excitation and spin of the compound nucleus, and include the competition of compound elastic and inelastic scattering and the variation of neutron widths from level to level.

Measurements of the radiative capture cross sec-

tions of ⁹⁸Mo, ¹³⁹La, ¹⁴¹Pr, ¹⁵⁸Gd, ¹⁷⁰Er, ¹⁷⁵Lu, and ¹⁷⁶Yb have been completed, and these results have been given in previous reports (ANL-6925, p. 249, ANL-7055, p. 230, and ANL-7125, pp. 237-239). Measurements of the capture cross section of ⁸⁹Y were completed recently and the data are presented in Figure VI-1. Also shown in the figure are the theoretical results calculated on the basis of the model discussed above. Similar calculations have been made for each of the other seven nuclides, and all of these results are being prepared for publication. Examples of these calculations are shown in Figures VI-2 and VI-3, where good agreement is evident between the theoretical values and the experimental values reported earlier for capture cross sections of ¹³⁹La and ¹⁴¹Pr. Also shown in Figures VI-2 and VI-3 for comparison are the experimental data of Konks et al.,² Johnsrud et al.,³ Gibbons et al.,⁴ and Macklin et al.⁵

² V. A. Konks, Yu. P. Popov, and F. L. Shapiro, *Zhur. Eksp. Teor. Fiz.* **46**, 80 (1964).

³ A. E. Johnsrud, M. G. Silbert, and H. H. Barschall, *Phys. Rev.* **116**, 927 (1959).

⁴ J. H. Gibbons, R. L. Macklin, P. D. Miller, and J. H. Neiler, *Phys. Rev.*, **122**, 182 (1961).

⁵ R. L. Macklin, J. H. Gibbons, and T. Inada, *Phys. Rev.* **129**, 2695 (1963).

¹ A summary of this section is given on page 19.

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FIG. VI-1. Radiative Capture Cross Section of Yttrium-89.

108-9300 Rev. 1

FIG. VI-2. Radiative Capture Cross Section of Lanthanum-139.

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FIG. VI-3. Radiative Capture Cross Section of Praseodymium-141.

Work has also begun on determinations of the capture cross sections as a function of neutron energy for several other isotopes. Data have been obtained for ^{85}Rb , ^{86}Sr , ^{87}Rb , and ^{41}K for neutron energies between

about 0.2 and 2 MeV. Relative shapes of these cross sections as a function of energy have been determined, but absolute values for the cross sections have not yet been obtained.

B. CAPTURE-TO-FISSION RATIOS IN EBR-II (D. C. STUPEGIA, A. A. MADSON)

In calculating the breeding gain of a reactor, one needs to know the neutron spectrum of the reactor and the cross sections as a function of neutron energy. When such complete sets of such data are difficult or impractical to obtain, it is useful to obtain the ratio of the capture and fission cross sections of a species in an existing fast reactor spectrum. This quantity is directly useful in breeding gain calculations for that reactor.

Work is now in progress (see ANL-6925, p. 251) which will measure the ratios of the capture and fission cross sections of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu as a function of position in EBR-II.

Three of the EBR-II subassemblies, containing several of the uranium and plutonium samples, have received the required irradiation and have been removed from the reactor; one of these has been disassembled and its samples shipped back to Argonne. The rest of the subassemblies will be removed from the reactor during the next six months.

An order has been placed for samples of ^{238}Pu and ^{241}Pu for further capture-to-fission ratio measurement paralleling those outlined above. At the time that the present work was started, samples of these two isotopes were not available.

VII

Analytical Research and Development¹

(R. P. Larsen, R. J. Meyer)

A program for the development of analytical methods for the determination of burnup of fast reactor fuels and for the measurement of fast fission yields is being carried out by the Analytical Group. Although

the emphasis in this program is directed toward fast reactors, the analytical methods will be applicable to thermal reactors as well.

A. TOTAL RARE EARTHS FOR MONITORING BURNUP (R. J. MEYER, R. D. OLDHAM)

A method for determining burnup by means of a total rare earth analysis is under development. After the rare earths are separated from interferences, a photometric EDTA titration is performed using arsenazo as the indicator. The advantages of and prerequisites for this method of burnup analysis, as well as a more detailed description of the titration, have been reported in ANL-7125, p. 241. The results reported there indicate that, providing a satisfactory procedure for separating interferences can be established, 500 μg of rare earths (200 mg of fuel, 1% burnup) can be determined with an accuracy of $\pm 0.5\%$.

Since several of the other elements present in an irradiated fuel, e.g., uranium, zirconium, and yttrium will either form colored complexes with arsenazo or react with EDTA, the titration must be preceded by a separation which isolates the rare earths from these constituents. In addition, such anions as fluoride or phosphate, which form strong complexes with the rare earths, must be absent.

From the data obtained by Korkisch and Tera² it appears that the separation of rare earths from all interferences can be made by adsorbing the rare earths on Dowex-1 from a nitric acid-methanol solution and eluting them with dilute nitric acid. Practically, however, the separation of the rare earths from several

thousand times as much uranium would require an unwieldy ion exchange column, and it is planned, therefore, to develop a two-step separation. The first step will separate the bulk of the uranium; the second will isolate the rare earths.

The ion exchange procedure was demonstrated to be compatible with the rare earth-EDTA titration. Lanthanum, in a solution of 90 v/o methanol-10 v/o 5N nitric acid, was adsorbed on Dowex-1 $\times 8$ resin (nitrate form). After the column was washed with 330 ml of 90 v/o methanol-10 v/o 5N nitric acid solution, the lanthanum was eluted with 1N nitric acid. The solution was evaporated to dryness, treated with perchloric acid to remove organic material, and the lanthanum titrated. The results obtained on four determinations at the 500- μg level had a standard deviation of $\pm 0.6\%$, with no significant bias.

Because the separation of yttrium from the rare earths is particularly important, an experiment was carried out using yttrium-90 tracer to confirm the separation. It was demonstrated that greater than 99% of the yttrium passes through the column under the conditions in which the rare earths are retained.

A preliminary separation of the rare earths from uranium, in which the rare earth fluorides are precipitated using calcium fluoride as a carrier, is presently being investigated and shows great promise. Results thus far show that 200- μg quantities of rare earths can be recovered quantitatively, while less than 0.5% of

¹ A summary of this section is given on page 19.

² J. Korkisch and F. Tera, *Anal. Chem.* **33**, 1264 (1961).

the uranium which was originally present is coprecipitated. The compatibility of this precipitation with the

ion exchange separation and EDTA titration remain to be investigated.

B. DETERMINATION OF THE FAST FISSION YIELD OF PRASEODYMIUM-141 BY NEUTRON ACTIVATION ANALYSIS (R. J. MEYER, K. K. PILLAY³)

Praseodymium-141 (stable) is a potentially useful burnup monitor for both fast and thermal reactor fuels. The fission yield is high, the half lives of its volatile precursors are short, and it is not a constituent of virgin or reprocessed fuels. However, neither the fast nor the thermal fission yield of this isotope has been measured. Of the various analytical techniques which have been used previously to determine fission yields, e.g., mass spectrometry, spectrophotometry, and radiochemistry, none is applicable to the determination of praseodymium-141. Thermal yields of the parent nuclide cerium-141 (31 days) have been published, but uncertainties in the decay scheme of cerium-141 and inaccuracies in establishing the number of fissions which produced this cerium nuclide make the values questionable. Neutron activation followed by gamma spectrometry, a technique that affords a means of high sensitivity and high specificity, is presently being investigated (ANL-7125, p. 242) for the determination of the fission yield of praseodymium-141.

The essential steps in the neutron activation analysis for praseodymium-141 in reactor fuels are as follows:

- (1) Dissolution of fuel sample.
- (2) Separation of the rare earths from uranium and plutonium.
- (3) Separation of the rare earths from other fission products.
- (4) Separation of praseodymium-141 from other rare earths.
- (5) Neutron activation of praseodymium-141 along with a flux monitor, manganese-55.
- (6) Chemical separation of impurities such as sodium introduced from reagents.
- (7) Gamma spectrometric analysis for praseodymium-142 and manganese-56.

Although several methods have been reported in the literature to accomplish any one of the chemical separation steps mentioned above, the following separations have been chosen to achieve minimum handling of hot samples, minimum contamination of the praseodymium with other nuclides that would also be activated, and maximum recovery of the praseodymium.

(1) Fuel samples are dissolved by refluxing the samples with *aqua regia* ($\text{HCl}:\text{HNO}_3$, 4:1) containing 1% hydrofluoric acid.

(2) Uranium and plutonium are separated by making the sample 8M in HNO_3 and extracting repeatedly with a 30% solution of tri-n-butyl phosphate solution in carbon tetrachloride. (Four extractions of this type provide a decontamination factor of approximately 10^5 for solutions which originally contain 1 g of uranium.)

(3) A fluoride precipitation using lanthanum as a carrier and hydrofluoric acid as the precipitating agent separates rare earths from all other fission products except yttrium, ruthenium, and a small percentage of zirconium. Any phosphate present from the extraction is also removed in this precipitation. Fuming of the fluoride precipitate with sulfuric and perchloric acids removes all of the ruthenium and fluoride.

(4) Praseodymium is separated from yttrium and most of the other rare earths using an ion exchange column packed with Zeolite-225 $\times$ 10 or Ag-50 W $\times$ 12 (20 to 30 μ) resin and eluting with a mixture of 0.2M α -hydroxyisobutyric acid and 0.2M ammonium α -hydroxyisobutyrate. The column is operated at 85°C. The praseodymium fraction contains approximately 1 to 2% of the cerium and neodymium that were originally present. The praseodymium fraction is easily identified by monitoring the praseodymium-144 (17 min) activity which is continually growing in from cerium-144 (285 day). Figure VII-1 shows a typical separation obtained on an irradiated sample of mixed rare earths using this ion exchange method.

To separate the praseodymium from residual cerium-144 activity, a technique developed at Hanford⁴ for recovering cerium-144 from processing wastes was modified for laboratory use. This technique uses an oxidation-anion exchange column which is packed with a mixture of Dowex-1 and lead dioxide. In 8N nitric acid cerium (III) is oxidized to cerium (IV) by lead dioxide and cerium (IV) is strongly adsorbed by the Dowex-1. Figure VII-2 shows a separation obtained using radioactive cerium and praseodymium

³ Resident Research Associate.

⁴ F. W. Roberts, Private Communication.

Thus, the eluant contains only praseodymium, 1–2% of the neodymium, and milligram quantities of lead.

(5) The internal flux monitor, manganese-55, is added and the samples and standards (known mixtures of praseodymium and manganese) are irradiated.

The desirability and advantages of internal flux monitors in activation analysis were discussed in ANL-7125, p. 242; precisions of $\pm 1\%$ were reported for praseodymium determinations in which sodium was used as the monitor. Unfortunately, large amounts of sodium are introduced from the laboratory reagents used in the above separation procedures, and it was therefore necessary to seek another flux monitor. Manganese-55 has proved to be quite satisfactory. Its cross section is reasonably high (13 barns) and it has no resonance peaks. The activation product has a practical half life (2.6 hr), and the principal gamma (0.845 Mev) does not interfere with the gamma (1.57 Mev) of praseodymium-142.

(6) The praseodymium and manganese are precipitated using a mixture of ammonium chloride, ammonium hydroxide and ammonium persulfate. This

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FIG. VII-1. Cation Exchange Separation of Rare Earths Using α -Hydroxyisobutyric Acid.

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FIG. VII-2. Separation of Praseodymium-142 and Cerium-144 on a Dowex-1, Lead Dioxide Column.

separation removes sodium activity (from reagents) which would otherwise interfere with the gamma spectrometry of praseodymium-142.

(7) The irradiated samples and standards are gamma-assayed for manganese-56 (0.845 Mev) and praseodymium-142 (1.57 Mev), and the weight of praseodymium-141 in the sample calculated.

Standard mixtures of praseodymium and manganese were irradiated to demonstrate the reliability of the detection system. The results on samples containing 120 to 200 μg of praseodymium showed a precision of $\pm 0.7\%$. On samples containing 20 to 30 μg of praseodymium the precision was $\pm 2\%$.

Samples of synthetic uranium fuel containing the major fission product elements in amounts that approximate 0.3% burnup have been analyzed using this procedure. Approximately 90% of the praseodymium present was recovered; the irradiated samples were free of contamination.

Since it is not anticipated that the procedure can be refined sufficiently to insure 100% recoveries of the praseodymium, a radiometric yield determination will

be made. Praseodymium-142 tracer of a high and known specific activity will be spiked into the sample before the first step in the separation procedure and the activity of the praseodymium solution measured after the cerium separation step. The fraction recovered will

be the ratio of praseodymium in the separated sample to the activity of a sample which has decayed the same length of time.

Application of the procedure to irradiated fuels will be initiated shortly.

C. URANIUM-235 THERMAL FISSION YIELDS OF CESIUM-133, CESIUM-137, AND TECHNETIUM-99

Values for the uranium-235 thermal fission yields of cesium-133, cesium-137, and technetium-99 were previously reported in ANL-6900, pp. 339-340. Additional data have allowed refinements to be made in these

calculations. The revised values are: cesium-133, $6.65 \pm 0.07\%$; cesium-137, $6.22 \pm 0.04\%$; technetium-99, $6.03 \pm 0.08\%$.