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CHEMICAL ENGINEERING DIVISON
RESEARCH HIGHLIGHTS

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RESUME OF THE ACTIVITIES OF THE
CHEMICAL ENGINEERING DIVISION
ARGONNE NATIONAL LABORATORY

GENERAL

The Chemical Engineering Division's program consists of work in the following areas: (1) development of processes and equipment for the recovery of fissionable and fertile materials from spent nuclear fuels, (2) development of methods for the synthesis and production of nuclear reactor fuels and materials, (3) studies of methods for the direct conversion of heat into electricity, (4) studies of the chemical and physical behavior of nuclear reactor fuels and materials suitable for use at high temperatures, (5) basic studies of unit operations, heat transfer, and mass transfer in nonaqueous systems, (6) basic studies of the chemistry of substances that are of interest to nuclear technology, but which are also providing fundamental data of importance to the scientific community, (7) studies of chemical reactions that are important to the safe handling of nuclear fuels and the safe operation of nuclear reactors, and the correlation of laboratory-derived data with conditions existing in nuclear reactors, (8) determination of nuclear constants, particularly neutron cross sections of elements that are of importance to the design and performance of fast breeder reactors, and (9) analytical chemistry in support of the research and development programs.

I. PYROMETALLURGICAL PROCESSES

Pyrometallurgical processes are being developed in order to achieve rapid recycle of high-burnup reactor fuels. These processes utilize high temperature separations in which the fuel is either maintained in the metallic state or subjected to a minimum of dry chemical conversions to oxides or halides. Liquid metals and salts are frequently used as solvents.

With such processes, low fuel recycle costs are expected to result from reduction in fuel inventories, avoidance or simplification of chemical conversions, small process volumes (and, hence, compact processing equipment), direct production of solid wastes, decrease in criticality problems because of the absence of aqueous solutions, and possible retention of valuable fuel alloying elements. Because of these characteristics, pyrometallurgical processes are particularly suited to processing of fast breeder reactor fuels in plants located on the reactor site.

The major objectives of these processes are repair of irradiation damage and restoration of the nuclear reactivity of the fuel. In contrast to solvent extraction and fluoride volatility processes, pyrometallurgical processes do not provide high removal of fission products. Removal of fission products is often just sufficient to maintain satisfactory nuclear and metallurgical properties of the fuel. Because of the resulting high residual activity levels, the development of procedures for remote refabrication of fuel elements is necessary. This is not considered to be a serious disadvantage because the concentrations of radioactive isotopes of fissionable and fertile materials would increase in extensively recycled fuel to an extent that would preclude direct handling of the fuel material even in the absence of fission products.

A processing facility (see Section I-D) has been constructed adjacent to the Second Experimental Breeder Reactor (EBR-II) in Idaho for the recovery of EBR-II fuels by means of pyrometallurgical processes that have been or are being developed by the Chemical Engineering Division. The first EBR-II fuel, an enriched uranium-fissium* alloy, will be recovered by melt refining, a simple melting procedure in which fission products are removed by volatilization and oxidative drossing reactions. Plant equipment for melt refining 10-kg batches of fuel has been installed in the EBR-II Fuel Cycle Facility and is being tested with nonirradiated fuel (see Section I-D).

*"Fissium" is a term which is used to denote collectively those fission product metals, such as molybdenum, ruthenium, rhodium, palladium, zirconium, and niobium, which are not removed from uranium by the melt refining process. In a fissium alloy, these metals are present in a ratio corresponding approximately to their yields in the fission process.

Two other processes are required in the EBR-II fuel cycle, one for recovering uranium-235 from melt refining crucible residues and the other for concentrating the plutonium bred into the uranium blanket material. In these processes, molten metals (e.g., zinc and magnesium) and molten halide salts are used as solvents. Other processes, which also utilize molten metal and salt media, are being developed for the recovery of future fast breeder fuels which contain plutonium. Metal, oxide, and carbide fuels can be accommodated in the liquid metal-salt processes.

A. Melt Refining Process

The first core loading of EBR-II consists of approximately 50% enriched uranium alloyed with 5% fissium. The fuel elements are made up of individual pins that are 0.144 in. in diameter and about 14 in. long. Each pin is clad with a 10-mil stainless steel jacket, which is thermally bonded to the fuel by a small amount of sodium in the annulus. To prepare the discharged fuel for processing by melt refining, the pins are declad mechanically and chopped to a convenient length (about 2 in.) for handling.

In the melt refining process, about 10 kg of the chopped pins is charged to a lime-stabilized zirconia crucible and melted; the molten metal is liquated at 1400°C for about three hours under argon (i.e., melt refined), and then poured into a mold. The furnace is heated inductively and is enclosed by a steel bell jar to permit the use of vacuum and a high-purity argon atmosphere. During melt refining, approximately two-thirds of the fission product elements are removed from the uranium by either volatilization or oxidation by the zirconia crucible. The oxidized fission products form a surface dross layer or deposit on the wetted crucible surfaces. Most of the volatilized fission products other than krypton and xenon are collected by condensation on a Fiberfrax* fume trap, which is inverted over the melt refining crucible. The oxidized fission products remain in the crucible in a skull, which is composed mainly of unpoured uranium metal and UO_2 . An auxiliary process utilizing liquid metal solvents (see EBR-II skull reclamation process) is employed to recover uranium from the skull material, which ordinarily amounts to 5 to 10% of the original melt refining charge.

The melt refining equipment for EBR-II has been installed in the Fuel Cycle Facility in Idaho (see Section I-D) and has been operated remotely with unirradiated fuel. During the past year, development work on the melt refining process and associated chemical operations in the Fuel Cycle Facility has included (1) further studies of the behavior of fission product iodine during melt refining, (2) the use of molten halide fluxes for the melt refining of uranium-plutonium fuel alloy, and (3) methods for the removal of nitrogen from the argon-atmosphere cell of the Fuel Cycle Facility.

*A molded product of the Carborundum Corporation prepared from amorphous fibers using a silicon dioxide binder. The principal constituents of the fibers are: Al_2O_3 , 51.2 w/o; SiO_2 , 47.4 w/o.

1. Fate of Iodine-131 in Melt Refining

Previous investigations had shown that over 99% of the fission product iodine is removed from the uranium-fissium fuel in the melt refining process (see ANL-6766, page 9). Although nearly all of the iodine activity that was recovered had condensed on cool surfaces near the melt refining crucible, apparently in the form of CsI, the over-all material balances for iodine were low (30 to 50%).

Because of the unknown fate of the balance of the iodine, two additional laboratory-scale experiments were performed with the objective of obtaining iodine distribution data together with satisfactory material balances. Twenty-gram pieces of uranium-fissium alloy were spiked with cesium (to represent fission product cesium), and with either KI or CsI, which were labeled with I^{131} . Each piece was melt refined for one hour at 1400°C in a zirconia crucible under an argon atmosphere in an induction-heated quartz tube furnace. (One hour of melt refining on this scale is about equivalent to three hours at full scale, because of the much larger surface-to-volume ratio in the small-scale operations.) A closed tantalum tube was employed as a condenser for the volatilized iodine activity.

Within the analytical uncertainty, all of the iodine (99.7% for the experiment with KI and 106% for the experiment with CsI) was accounted for in both experiments. The distribution was the same as that found in the earlier work, that is, over 99% of the iodine had volatilized and condensed, apparently in the form of a compound (probably CsI), on the tantalum condenser. In the plant equipment most of the fission product iodine will be condensed on the Fiberfrax fume trap with some condensation possibly occurring on the upper wall of the melt refining crucible. Unlike the crucibles used in the previous laboratory experiments, which were essentially isothermal at 1400°C, the plant crucible will have a significant temperature gradient, the upper portion being at temperatures as low as about 700°C. On the basis of the laboratory studies, it is expected that the distribution of fission product iodine in the plant melt refining equipment will be approximately as indicated in Table I-1.

Table I-1

EXPECTED DISTRIBUTION OF IODINE ACTIVITY IN FULL-SCALE EBR-II MELT REFINING PROCESS

Product Ingot	~0.3%
Skull	~1%
Off-Gases	<0.01%
Crucible and Fume Trap	~99%

At the completion of melt refining in the EBR-II process cell, it will be necessary to remove the Fiberfrax fume trap from the furnace and to transfer it to a container for storage. Because of fission product decay heat from the skull, the fume trap may have a temperature as high as about 700°C on the inner surface and 350°C on the outer surface at the beginning of the transfer operation, if the fume trap remains in a closed position on top of the crucible. When the fume trap is tilted away from the crucible as it is during pouring of the ingot, the temperature of the fume trap will decrease to about 170°C. Two laboratory experiments were performed to determine whether release of iodine activity from the fume trap to the argon atmosphere of the EBR-II process cell would become a significant problem at these temperatures. Uranium-fissium alloy spiked with I^{131} activity and with a small amount of sodium (to represent material from the thermal bond) was melt refined for one hour at 1400°C with a Fiberfrax plug on top of the zirconia crucible. The Fiberfrax was then transferred to a separate chamber in the apparatus where it was heated to simulate fission product decay heating and was exposed to a stream of argon moving at 6.6 ft/min, which is about the rate of flow of the argon atmosphere in the EBR-II process cell. The iodine activity was removed from the effluent argon for analytical purposes by means of activated charcoal-filter devices.

In the first experiment, in which the Fiberfrax was heated so as to have a gradient from 700°C to 300°C in the flowing argon, the iodine activity was released to the argon at a nearly constant rate of about 0.2% per hour over a 36-hr period. In the second experiment, with the Fiberfrax at 170°C, the release rate was about 10^{-3} of the rate at the higher temperature. Increasing the oxygen impurity level in the argon from 2.2 ppm to 175 ppm at this lower temperature raised the iodine release rate by a factor of only about 2.5.

The iodine will be released to the argon atmosphere of the processing cell, which has a volume of 65,000 cu ft. In connection with the operations of material transfer locks, a small portion of the cell gas (expected to be not more than 1000 cu ft per week) will be discharged through the suspect stack. Because of the large dilution of the iodine in the cell gas, in other gas discharged through the stack, and in the surrounding atmosphere, an off-gas handling problem would not be created by the low iodine release rates stated above, provided that the crucible and fume trap are canned within about one hour in air tight containers.

2. Use of Salt Fluxes in Melt Refining

Potential improvements in the melt refining processes may be provided by the use of halide salt fluxes. The advantages of melt refining beneath a molten flux layer are: short operating times (about 1 hr at temperature), low operating temperatures (about 1100°C), and high product yields (probably greater than 99% on full plant scale). The feasibility of this procedure was previously investigated on a 700-g scale with uranium-fissium alloys containing 0.5 to 0.8 w/o cerium (see ANL-6766, p. 11).

With a calcium chloride flux containing 7 w/o magnesium fluoride as a rare earth oxidant, excellent cerium oxidation and removal in the flux phase was realized in one hour at 1100 C to 1300 C without apparent attack on a beryllia crucible. Yields of purified metal were high (95 to 98%).

During the past year, preparations were made to evaluate this procedure for plutonium-containing fuels and a few preliminary experiments were performed. Because plutonium trichloride is only slightly less stable than rare earth chlorides, the point in question is whether a preferential oxidation of rare earths can be effected without simultaneous oxidation and loss of some plutonium to the flux phase. By careful control of the amount of magnesium fluoride (or chloride) oxidant to just slightly in excess of that required to oxidize the rare earth elements, preferential oxidation of rare earths and their extraction into the salt phase can be accomplished without significant oxidation and extraction of the plutonium should be possible. Experiments are being conducted in the melt refining furnace with attached glove box shown in Fig. I-1. For work with plutonium alloys, the composition of the carrier flux has been changed from CaCl_2 to 80 to 85 w/o BaCl_2 - balance CaCl_2 because the latter flux has a satisfactorily low melting point ($\sim 875^\circ\text{C}$), is readily separable from solidified metal, and has low volatility at operating temperatures.

Figure I-1

SCHEMATIC DIAGRAM OF INDUCTION FURNACE AND GLOVE BOX FOR MELT REFINING OF URANIUM-PLUTONIUM-FISSIUM ALLOY

Two experiments have been completed with alloys containing 10 w/o plutonium, 10 w/o fissium, and 80 w/o uranium to determine plutonium losses by volatilization or by extraction of PuCl_3 into the flux: (1) a blank experiment (i.e., with no rare earth oxidant present) and (2) the first of a series of runs with oxidant present. In the blank experiment, plutonium losses were low, only 0.05% by evaporation and 0.09% by extraction. In the other experiment, in which a MgCl_2 oxidant was employed at a concentration that was 10% in excess of that required for oxidation of the rare earths, plutonium losses by extraction and volatilization were 0.45% and $<10^{-3}\%$, respectively. These, too, are encouragingly low losses. If similarly low losses prevail in future runs, it may be concluded that the flux melt refining procedure has merit. One of the important remaining problems would then be the procurement of plant-size beryllia crucibles.

3. Removal of Nitrogen from Argon with Titanium Sponge

A method is under development for removing nitrogen from argon by gettering the nitrogen on hot titanium sponge metal. Although this method will have general utility, the major incentive for its development is a possible future need to remove nitrogen from the argon atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility (see Section I-D). The equilibrium nitrogen concentration in the atmosphere of the Argon Cell is expected to be about 5 v/o. Two sets of experimental equipment have been constructed for the nitrogen-removal study: (1) equipment for determining the kinetics of nitrogen removal from argon on hot titanium sponge, and (2) a pilot plant for obtaining overall process performance data and information on component reliability. Studies are being conducted with argon containing initial nitrogen concentrations between 50 and 50,000 ppm.

a. Kinetics of Nitrogen Removal from Argon with Titanium Sponge

A gas-circulating loop has been built for a study of the kinetics of nitridation of titanium sponge by argon-nitrogen mixtures. Operating principles of this loop were described in ANL-6766, p.14. In this equipment an argon-nitrogen mixture of carefully controlled composition is continuously circulated through a series of eight small (3-g) test beds containing titanium sponge. The circulation rate (50 to 1500 liters/hr) is such that only a very small fraction of the nitrogen present in the gas stream reacts with the titanium in a single pass through the series of beds. The purpose in maintaining the circulation rate such that only a small fraction (less than 5%) of the nitrogen present in the gas stream reacts during any given pass is to approximate a differential titanium bed in order to facilitate interpretation of the data. The extent of reaction of the titanium test material is determined at intervals during the run by successively and permanently removing the topmost titanium bed and determining its nitrogen content by a Kjeldahl analysis.¹ For analysis of the data, it will be assumed that each test bed in the series reacted with gas having the same nitrogen concentration.

¹Thompson, J. M., Anal. Chem., 25, 1231-5 (1953).

Preliminary Performance of the Experimental Equipment.

In preliminary operation of the gas circulating loop, the ability to maintain gas circulation rates and nitrogen concentrations to within 1% of the desired values has been routinely demonstrated. Despite this ability, satisfactory operation of the loop has not yet been demonstrated. The major difficulty has been the achievement of a differential bed. Reaction rates have been low in the first few beds. These low rates are believed to have resulted from two possible causes. (1) The incoming gas has not been sufficiently preheated to bring its temperature up to 900°C. As a result, the first few beds have operated at temperatures slightly below 900°C and have served partially to bring the gas up to the desired operating temperature of 900°C. To overcome this problem, an additional gas preheater consisting of a packed bed has been installed in front of the series of test beds and measurements of the temperature of the gas entering the test beds are being made by radiation-shielded thermocouples. (2) Gettering of oxygen contamination in the first few beds may have formed an oxide film on the titanium sponge in these beds. Such a film is known to interfere with the titanium-nitrogen reaction.^{2,3} However, oxygen contamination is not believed to have been a serious problem since, from the oxygen content of reacted sponge, the oxygen concentration in the argon gas was calculated to be <6 ppm. In the event that oxygen contamination should prove to be a problem, an oxygen-gettering bed will be installed in front of the series of test beds. Ultimately, the effect of oxygen will be determined by deliberately adding known amounts of oxygen to the circulating argon gas.

In this preliminary work, reaction rates have been such that about 18% conversion of the titanium sponge (calculated on the assumption that TiN is formed) has occurred in 24 hours with argon containing 1000 ppm nitrogen. Reaction rates were essentially the same for two fractions of sponge particles, one, 0.072 ± 0.007 in. in diameter, the other, 0.148 ± 0.054 in. in diameter, which were used alternately in the series of eight beds. This result indicates that the size of the sponge particle is not an important variable.

b. Pilot Plant for Nitrogen Removal from Argon

The pilot plant scale unit, which was built to provide information on component design and reliability for large volume purification systems, has recently been placed in operation. In the pilot plant unit, argon containing nitrogen in concentrations from 50 to 50,000 ppm is circulated at a rate near 10 cfm. As shown by the equipment layout of the unit (Figure I-2), the direction of gas flow through this titanium sponge bed is periodically reversed and regenerative heat exchangers are used alternately

²Gibbs, D. S., Svec, H. J., and Herrington, R. E., Ind. Eng. Chem., **48**, 289-296 (1956).

³Gulbransen, E. A., and Andrew, L. F., Trans. AIME, **185**, 741-748 (1949).

to cool the gas exiting from the titanium sponge bed and to preheat the incoming gas.

Figure I-2

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

The pressure drop through the system is about 1.4 psi. The blower used to circulate the gas operates at inlet pressures of from 0 to 2 psig and, by variation of the blower speed, at outlet pressures of from 1 to 12 psig. At the system pressure drop, the circulation rate can be varied from 0 to 50 cfm. The blower is of special design to prevent air and oil leakage into the circulating gas.

The high temperature vessels of the pilot plant (the trickle heaters and the titanium sponge reactor) were fabricated of Hastelloy "X"* because of its high temperature strength. However, the Hastelloy "X" tank containing the titanium sponge is lined with Type 316 stainless steel because of the latter's superior resistance to reaction with the sponge. All other vessels in the system are fabricated of Type 310 stainless steel. Presented in Table I-2 are the results of 400-hour tests made to evaluate various Inconel, stainless steel, and Hastelloy alloys for the containment of titanium sponge at 900°C.

*Trade name of Haynes Stellite Division of Union Carbide.

Table I-2

CORROSION OF INCONEL, STAINLESS STEEL,
AND HASTELLOY ALLOYS BY TITANIUM SPONGE

Test Conditions

Time: 400 hours

Temperature: 900°C

Atmosphere: argon

Charge: 1/4-inch particles of solid titanium sponge (99.4% Ti, melting point 1800°C). The particles were placed on or in contact with a coupon of the material under test in an alumina crucible.

Static conditions

<u>Material</u>	<u>Depth of Reaction Zone^a</u> (mils)
Inconel 702	3 to 4
Inconel 718	3 to 4
Inconel 750	4 to 5
Inconel 800	3 to 4 ^b
Stainless Steel Type 304	4 to 5 ^b
Stainless Steel Type 310	2 to 4 ^b
Stainless Steel Type 316	<1 ^b
Hastelloy C	5 to 7
Hastelloy X	5 to 7

^aAt the conclusion of each test, particles of the titanium sponge adhered to all of the coupons. The depth of the reaction zone was measured in the area of adherence.

^bIn addition to a reaction layer, grain boundary precipitation of an unidentified phase was observed.

B. Processes Employing Liquid Metal Solvents

Work was continued on several liquid metal processes which are being developed for the recovery of spent reactor fuels. The processes under development are (1) a skull reclamation process for the recovery and purification of the fissionable material in melt refining crucible residues (skull material), (2) a blanket process for concentrating the plutonium bred in the EBR-II blanket material, and (3) processes for advanced core materials which contain plutonium as the fissionable material. Both the skull reclamation and blanket processes are now being studied on a pilot plant scale. The advanced core processes are in a laboratory stage of development, but engineering development of these processes has been started. Methods of reprocessing ceramic fuels by pyrometallurgical procedures are also being studied.

Development of these processes has been supported by fundamental studies of liquid metal and salt systems. These include basic chemistry studies, the development of physical property data, and engineering studies on distillation, heat transfer, mass transfer, and mixing in metal systems.

1. Skull Reclamation Process

The skull reclamation process is an adjunct to the melt refining process in the EBR-II fuel cycle, and has been developed to recover uranium from melt refining crucible residues. The process must effect a separation of uranium from noble metal fission products (zirconium, molybdenum, ruthenium, and technetium) that are not removed in melt refining and from rare earth and alkaline earth fission products that are removed from the bulk fuel material in melt refining by concentrating them in the skull material.

A flowsheet of the skull reclamation process is presented in Figure I-3. The skull reclamation process has not been changed significantly since its presentation in ANL-6766, p. 17. However, three major changes have been made in the method of operation. The first major change is that the steps between skull oxidation and retorting are now conducted in a single large tungsten crucible (12 in. OD by 19 in., weighing 500 lb). A large beryllia crucible, made by a thixotropic casting procedure and having about the same dimensions as the tungsten crucible, was to have been used for the uranium precipitation steps. However, two such large beryllia crucibles were wetted by the metal solutions, thereby preventing removal of a uranium product cake or concentrate for retorting. The failure of these beryllia crucibles to perform as expected made it necessary to carry out the uranium precipitation steps in the tungsten crucible. Fortunately, this change in procedure proved to be not only feasible, but also attractive, since it has the considerable advantage that one entire bell jar and furnace system (that used for a beryllia crucible) is eliminated from the processing equipment.

Figure I-3

FLOWSHEET OF THE EBR-II SKULL RECLAMATION PROCESS

(*The waste flux can be removed after either the reduction of uranium oxides or decomposition of the intermetallic compound. The decision will depend on the results of current investigations.)

The second change is necessitated by the first. Because the residual magnesium-zinc solution wets tungsten, it is not possible to remove a solid uranium concentrate from a tungsten crucible. Therefore, it is necessary to dissolve the uranium product in the tungsten crucible and to transfer the solution (or possibly, an ingot cast from the solution) to a small beryllia retorting crucible. A beryllia crucible or a beryllia-lined crucible will still be used as the retorting crucible because of the ability of beryllia to contain magnesium-zinc solutions and because of high resistance to attack by molten uranium, the product of the retorting operation. The quantity of solvent to be evaporated per kilogram of uranium would be 0.4 to 1 kg for a uranium concentrate (a 50 w/o magnesium-zinc alloy) but will be a minimum of 7.3 kg for uranium in solution in a 12 w/o magnesium-zinc alloy. The larger-volume retorting operation has been carried out in the absence of uranium in equipment designed to be installed within the bell jar of a melt refining furnace. Because uranium was not present in this work, the retorting step cannot be regarded as having been demonstrated.

The third change in procedure, which is being currently investigated, is to delay the removal of the flux from the crucible until after the metal waste solution from the decomposition step (Fig. I-3) is removed. Previously, the flux was transferred out of the crucible after the reduction operation. Transfer of the waste flux at this point required raising the transfer line so that its open end was just above the flux-metal interface.

By delaying the transfer of flux, the transfer line can remain in a fixed position, thereby simplifying remote operation.

During the past year, small-scale (100 to 150 grams of uranium) demonstration runs of the skull reclamation process were completed, and considerable work was carried out in pilot plant equipment (about 1.5-kg-uranium scale). Design of a plant equipment mock-up was begun. This plant equipment will be installed later in the EBR-II Fuel Cycle Facility.

a. Small-Scale Demonstration Runs

The small-scale demonstration runs were made to establish permissible ranges in process conditions and to expose and rectify any process difficulties. Results of the small-scale runs show that the following process performance may be expected:

Uranium Recovery ~ 95%

Losses

Skull Oxidation	2.5%
Noble Metal Extraction	0.05%
Reduction	0.5%
Intermetallic Compound Precipitation	1 to 2%
Intermetallic Compound Decomposition	<u>0.4 to 0.7%</u>
Total	4.4 to 5.8%

Fission Product Removals

Rare Earths	90%
Ruthenium	80%
Molybdenum	90%
Palladium	99%
Zirconium	75%
Barium and Strontium	99%

Since less than 10% of the total EBR-II fuel is processed in the skull reclamation process, the approximately 95% yields are adequate and would result in overall uranium recoveries of greater than 99.5%. The fission product removals are sufficient to maintain the desired concentrations of the fission alloying elements (ruthenium, molybdenum, zirconium, and palladium) in the EBR-II fuel.

Special skull reclamation process problems which were studied are the following:

- 1) Efficiency of Skull Removal from Melt Refining Crucibles. The first step in the skull reclamation process is oxidation of the skull material in a melt refining crucible and subsequent removal of the oxide powder by pouring. This step has been demonstrated in prototype skull oxidation and oxide dumping equipment built in the fuel cycle mock-up facility. The efficiency of uranium removal from plant-size zirconia crucibles has been determined during the past year by pulverizing ten waste crucibles and analyzing samples for uranium by X-ray fluorescence. The amount of uranium retained in the waste crucibles averaged 2.5% and ranged between 1 and 3.5% of the initial amount in the skull. These results are higher than results previously obtained by acid leaching of uranium from the waste crucibles. Apparently, not all of the uranium was removed by the acid leaching procedure. A loss of 3.5% in waste crucibles is equivalent to a loss of less than 0.35% of the total uranium being processed.
- 2) Zirconium Behavior. Although removal of zirconium has generally been satisfactory, the behavior of zirconium has often been erratic and has not been understood. Therefore, further study of zirconium behavior is in progress.
- 3) Sampling of Metal Solutions for Ruthenium Analysis. Ruthenium in metal solutions has been found to interact with or absorb on tantalum sampling tubes and filter frits. Since a satisfactory substitute for tantalum is not available, it has been necessary to change the sampling procedure. Bucket-type samples are now taken in tantalum tubes and chilled quickly. With this procedure, the percentage of ruthenium removed from the sample by interaction with the sample tube has been reduced to an acceptable level, between 2 and 6%.

- 4) Handling of Non-Decladable EBR-II Fuel Pins. A brief laboratory study showed that any EBR-II fuel pins of the first core that are not mechanically decladable, and therefore are not amenable to processing by melt refining, can be accommodated in the skull reclamation process. The type 304 stainless steel cladding on the first core fuel pins is readily dissolved in zinc, as is the contained fuel material. The uranium may be subsequently transferred from the metal phase to a molten halide salt phase by oxidation to uranium trichloride. The feasibility of recovering uranium from other non-soluble or low-solubility cladding materials, such as tungsten or a niobium-1% zirconium alloy, by a "chop-leach" procedure was also shown. In this procedure, the uranium is removed from chopped segments of the clad fuel by dissolution of the uranium in a suitable solvent, such as molten zinc.

b. Pilot Plant Studies of the Skull Reclamation Process

A pilot plant for the skull reclamation process is currently being operated for equipment- and process-demonstration purposes. The scale of operation in the pilot plant is about 2 kg of skull oxide (about 75% is uranium); the EBR-II plant scale is about 7 kg of skull oxide.

A description of the pilot plant was given in ANL-6766, p.23. Because the process steps are now being conducted in a single large tungsten crucible, only one of two available bell jar furnaces is employed in a run. The second bell jar furnace, which is now a spare, is used for testing equipment and materials and for remelting waste metal ingots for sampling. A cross-sectional view of one of the bell jar furnaces is shown in Fig. I-4. The tungsten crucible is centrally located within the bell jar, which is 24-in. OD by 32 in. high. Surrounding the tungsten crucible are a graphite susceptor, a Fiberfrax insulator, and a copper induction coil. Enclosure of the furnace within a bell jar allows an argon atmosphere to be maintained in the system and permits pressurization of the furnace for transfer of molten metals or salts through a pipe to a waste container or, in the case of the product solution, to a retorting crucible. The bell jar cover has three nozzles: one accommodates a stirrer, the other two are employed for insertion of transfer pipes and other equipment used for sampling, liquid-level measurements, and temperature measurement.

The bell jar furnaces are presently being operated in an open glovebox. Eventually, the glovebox will be closed, and an argon atmosphere or nitrogen atmosphere will be maintained within it.

Equipment Performance. To date, eight runs have been made in the pilot plant. In these runs, development of reliable operating procedures and improvement in equipment performance have been

Figure I-4

BELL JAR FURNACE FOR SKULL RECLAMATION PROCESS

emphasized. During the course of these runs, the three major operating changes described at the beginning of this section were evolved (use of a single tungsten crucible, use of a fixed transfer line, and removal of the uranium product in a metal solution). In general, the equipment has operated satisfactorily. However, difficulties with the transfer tubes have been experienced with heater failures and with plugging of tubes. Since startup of the pilot plant, the operation of the transfer tubes has been improved considerably by design and operational changes, but before the transfer operation can be considered sufficiently reliable for remote operation, further improvements must be made, together with demonstrations of trouble-free operation for long periods of time.

The following improvements in equipment design and operation have been made:

- 1) Mechanical mixing has been improved to the point where the reduction of uranium oxides appears to be complete within one hour. A small-scale study, which is described later, is now underway in special equipment to relate reduction rate with mixing power input. Work on induction mixing has been discontinued because mechanical mixing provides better contacting of the metal and salt phases.
- 2) A method suitable for the remote sampling of metal and salt solutions has been devised. In this method, a sample of liquid metal or flux is drawn by vacuum through a 1/16-in. hole located one-third of the way up the side of a closed-bottom, 1/4-in. OD by 4-in. long tantalum tube. The tube is swaged onto the end of a long steel capillary tube which is connected to a small vacuum reservoir through a valve.
- 3) An eddy-current induction probe is under investigation for remote determination of molten metal levels and possibly molten salt levels. The probe consists of dual-wound, primary and secondary, nichrome coils on a ceramic core. The output of the secondary coil is strongly affected by the presence of a surrounding conductor. A particular advantage of the eddy current induction probe is that it operates within a well similar to a thermocouple well; therefore, it may be easily removed for repair or replacement.

With the present skull reclamation furnace, from 4 to 6 hours are required to cool a crucible and its contents from 800°C to the transfer temperature of 425 to 525°C even though cooling is hastened by circulating argon gas through the furnace and a water-cooled heat exchanger. To improve the cooling characteristics of the furnace, a new design is being

considered for the EBR-II plant equipment which involves placing the tungsten crucible in a tight-fitting steel vessel, and locating the insulation and induction coils at the outside of the steel vessel. The insulation would be removable, thus allowing cooling by radiation.

The available chemical results indicate the process performance (uranium recovery and fission product removal) to be similar to that realized in the small-scale demonstration runs with one exception, namely, a low removal of noble metal fission products in the pilot plant. This probably has resulted from insufficient mixing in the noble metal extraction step.

Future Work. Operation of the skull reclamation pilot plant will be continued until the necessary techniques and equipment have been developed for reliable operation of the equipment, or similar equipment, by remote methods. In the course of this work, a series of about five process demonstration runs will be made.

The removal of the product uranium from the tungsten crucible in metal solution, rather than from a beryllia crucible in a solid cake or concentrate as was previously envisioned, has necessitated changes in the retorting step. As pointed out previously, the volume of materials to be handled is about tenfold greater. In order to permit retorting of uranium-bearing solutions, a bell jar furnace is now being installed within an inert atmosphere box. The retorting operation will be conducted in a beryllia crucible. Since retorting is also necessary in the advanced core processes, a program for the long-range development of retorting equipment has been initiated.

2. Blanket Process

The objective of the blanket process for discharged EBR-II blanket material is to concentrate the plutonium from its initial concentration of 1 w/o to a value of at least 40 w/o in uranium so that it may be used for enrichment of core materials. The blanket process has not been changed during the past year from the flowsheet shown in Figure I-5. In this process, blanket material is dissolved in a 12 to 14 w/o magnesium-zinc alloy to produce a 12 to 14 w/o uranium solution. The subsequent addition of magnesium to an approximately 50 w/o concentration precipitates the uranium from solution while the plutonium remains in solution. By cooling to about 425°C, the uranium solubility in the supernatant phase is further decreased, and then the plutonium-bearing supernatant phase is removed. Isolation of the plutonium from this latter phase is to be accomplished by evaporating the magnesium and zinc.

The blanket process up to the evaporation of solvent metals from the plutonium product solution was demonstrated in a series of runs which were reported in ANL-6766, pp. 27-30. In these runs, the percentage of plutonium separated from the bulk uranium (which would be recycled)

varied between 92 and 100%, and the ratio of plutonium to uranium in the product solution (prior to evaporation) was such that the plutonium concentration in uranium would have been between 44 and 70 w/o after evaporation of the solvent metals. The first two steps of this process will ultimately be conducted on a 5-kg uranium scale in the skull reclamation process pilot plant when work on the latter process has been completed. However, these two steps are essentially the next to the last two steps of the skull reclamation process, and, in effect, are being thoroughly demonstrated on a large scale. Therefore, blanket process operations in the pilot plant are likely to be service operations for producing product solutions for study of the evaporation step.

Figure I-5

SCHEMATIC FLOWSHEET OF THE EBR-II BLANKET PROCESS

The concentrations of plutonium and uranium in the 50 w/o magnesium-zinc supernatant from the uranium precipitation step are about 0.08 w/o and 0.05 w/o, respectively. The plutonium will be concentrated to between 1 and 10 w/o by evaporating most of the magnesium and zinc. Preliminary work on this evaporation step was begun in the past year using product solutions containing either cerium or tin as a stand-in for plutonium. Tin became the preferred substitute because both tin and plutonium are liquids at still-pot temperatures of 710 to 770°C, while cerium is not. The simulated evaporation runs were conducted on an 8 to 10-kg scale in an induction-heated tantalum still-pot that was 8-3/4 in. in diameter and 18 in. high.

In early runs with cerium or tin present as a nonvolatile solute element, it was found that a large percentage of these solutes (about 30%) was deposited as a film on the still-pot wall. In these runs, the temperature of the exposed wall of the still-pot was higher than that of the boiling metal. Consequently, magnesium and zinc were "flashed" from any solution that splashed or spattered onto the still-pot wall above the solution level, leaving behind a deposit of cerium or tin. In later runs with tin (at 0.5 w/o concentration), the induction coil was positioned near the bottom in an effort to

reduce the temperature of the exposed wall, in order to, through partial condensation of the metal vapors, dissolve or wash back into the liquid any solute which may have deposited on the wall. With such induced reflux, deposition of tin on the still-pot walls and on baffles located in the vapor space was only 2% or less of the total tin charged, even when the evaporation was taken to near dryness. This principle of reflux within the still-pot is being incorporated in the design of an improved distillation unit.

3. Process for Uranium-Plutonium Fuels

Fuels that contain mixtures of uranium and plutonium are being developed for use in fast power breeder reactors. Metals, carbides, oxides, and other forms of these elements are receiving consideration. It appears that liquid metal processes might profitably be applied to these fuel materials, using demonstrated separation techniques such as molten salt extraction and precipitation from liquid metal solutions. The overall objectives of a process of this type are to remove fission products from the spent fuel and to recover the uranium and plutonium in high yield and in a form that is suitable for refabrication into new fuel elements.

The development of these fuels is in a relatively early stage, both for future plutonium loadings of EBR-II and for other fast breeder reactors. Insufficient information is available on specific fuel compositions and cladding materials to attempt the development of a detailed process flowsheet at the present time. Instead, the development effort has been focused on basic separations that would be common to a variety of flowsheets. For purposes of illustration, however, a conceptual process for a metallic breeder reactor fuel is shown in Figure I-6. In this case, the fuel would first be dissolved in liquid zinc, releasing the rare gas fission products. The uranium and plutonium would then be oxidized by zinc chloride and extracted into a molten chloride flux, while the noble

Figure I-6

CONCEPTUAL PYROMETALLURGICAL PROCESS FOR URANIUM-PLUTONIUM ALLOY FUEL

^aMetals such as vanadium, titanium, zirconium, tungsten.

metal fission products and refractory metal cladding material would remain in the zinc, which would be discarded as a waste. The salt would be contacted with a cadmium-zinc-magnesium solution, thereby reducing the uranium and plutonium, which would enter the metal phase. The rare earths and other electropositive fission product elements would be discarded with the salt. The metallic uranium and plutonium would then be recovered by vacuum distillation of the cadmium-zinc-magnesium solution.

The process development work described below includes studies of basic separation techniques and determinations of pertinent properties of liquid metal and molten salt systems. Also described is an alternative method for the separation of rare earths from uranium and plutonium, a method which entails selective precipitation of the uranium and plutonium from calcium-zinc solutions.

a. Solubility of Uranium in Cadmium-Zinc-Magnesium Solutions

In the EBR-II skull reclamation process and in earlier work on processes for uranium-plutonium fuels, the zinc-magnesium system was selected as the liquid metal solvent. However, in the present work on processes for uranium-plutonium fuels, the possibility of using a ternary system, zinc-magnesium with a high percentage of cadmium, is being investigated. The ternary system appears attractive because lower operating temperatures and decreased zinc concentrations may permit the use of series 400 stainless steels instead of tungsten or tantalum for process vessels. The principal criteria governing the choice of solvent composition are (1) adequate solubility of uranium and plutonium, (2) acceptable corrosion rates, and (3) distribution coefficients that will permit the desired separations by molten salt extraction. The objective of this study was to determine whether regions of composition exist in this ternary solvent within which the solubility of uranium is sufficiently high for process use.

To obtain the solubility data, excess uranium metal and the ternary alloy were held in a Morganite (recrystallized alumina) crucible inside a tantalum secondary vessel. This assembly was located inside a resistance-heated stainless steel furnace tube. Provisions were made to maintain a high-purity argon atmosphere, to control and measure the temperature to $\pm 1^\circ\text{C}$, to stir the solvent, and to withdraw liquid metal samples through tantalum filters into tantalum sample tubes. A layer of molten salt (LiCl-KCl eutectic, m.p. -350°C) on top of the liquid metal served to minimize vaporization of the metal and to decrease temperature gradients near the liquid metal surface. A minimum of six hours was allowed for equilibration at each temperature, and equilibrium was approached from both higher and lower temperatures. The samples were analyzed for uranium, magnesium, and zinc. Metallographic and X-ray data on quenched samples were also used, along with material balance information to characterize the solid uranium-bearing phases in equilibrium with the solution.

The solubility of uranium at 600°C is shown as a function of composition of the cadmium-zinc-magnesium solvent in Figure I-7. Two regions of high uranium solubility are evident, one at about 50 a/o Zn-50 a/o Mg, and the other at approximately 83 a/o Cd-17 a/o Zn. Since the uranium solubility is considerably higher in the latter region and the corrosion rate of stainless steel is lower because of the lower zinc concentration, this region is preferred for process use. However, in order to obtain suitable distribution coefficients for a molten salt extraction process, it is necessary that some magnesium, perhaps about 20 to 30 a/o, also be present.

Figure I-7

SOLUBILITY OF URANIUM IN
CADMIUM-ZINC-MAGNESIUM ALLOY AT 600°C

A typical curve showing the temperature coefficient of the uranium solubility in the cadmium-rich region is shown in Figure I-8. These data were obtained at a nominal composition of 80 a/o cadmium-10 a/o zinc-10 a/o magnesium. In the high temperature range (above ~570°C), a slightly retrograde solubility was observed, and metallic uranium was identified as the solid phase in equilibrium with the solution. In the intermediate temperature range (about 450 to 570°C), the uranium solubility showed a normal (nonretrograde) temperature dependence. The delta-phase uranium-zinc intermetallic compound ($\sim\text{UZn}_{8.5}$) was identified as the solid in this case. In the lower temperature range (below ~450°C), the temperature dependence of the uranium solubility is greater, and both the delta-phase uranium-zinc compound and UCd_{11} appeared to be in equilibrium with the solution.

Although higher uranium solubilities than those indicated in Figures I-7 and I-8 would be desirable, the measured solubilities are adequate for process purposes. At present, the solubility of plutonium is being determined in the composition regions in which high uranium solubilities were found.

b. Metal-Salt Distribution Studies

Determinations of the distribution coefficients of pertinent elements between liquid metals and molten salts have continued. The recent studies have been concentrated mainly on the effects of different compositions of the liquid metal and molten salt phases on the distribution coefficients. The equilibrium reaction involved in the distribution of an element, M, is

Figure I-8

TEMPERATURE DEPENDENCE OF URANIUM SOLUBILITY IN CADMIUM-ZINC-MAGNESIUM ALLOY

Nominal composition of solvent:

80 a/o Cd

10 a/o Zn

10 a/o Mg

The distribution coefficient, K_d , is defined as

$$K_d = \frac{(\text{w/o M in salt})}{(\text{w/o M in metal})}$$

The distribution coefficients were determined experimentally by adding the element under investigation to either the salt or metal phase and mixing the phases under an argon atmosphere in a tantalum crucible at the selected temperature. Equilibrium was approached from both directions by increasing and decreasing the magnesium concentration in the metal phase. Filtered samples of the two phases were withdrawn and analyzed by chemical or radiochemical methods. Equilibrium was reached within the first few minutes in the systems studied.

Figure I-9 shows the effect of variation in the composition of the metal phase on the distribution of praseodymium between 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂ and cadmium-zinc-magnesium solutions at 600°C. The praseodymium was activated by irradiation so that it could be conveniently

analyzed by counting the characteristic gamma emission of praseodymium-142. Praseodymium was used because it is the most difficult of the major rare earth fission products to separate from uranium and plutonium.

Figure I-9

DISTRIBUTION OF PRASEODYMIUM
BETWEEN NaCl-KCl-MgCl₂
MOLTEN SALT AND CADMIUM-
ZINC-MAGNESIUM ALLOY

Conditions

Temp: 600°C
Crucible: tantalum
Atmosphere: argon
Salt: 30 m/o NaCl-20 m/o
KCl-50 m/o MgCl₂

It is expected that in a practical separation process, a salt:metal weight ratio of about 1:2 would be used. Therefore, for optimum separation of rare earths from uranium and plutonium, it is desired that the distribution coefficients for the rare earths be greater than 2.0, and that those of uranium and plutonium be less than 2.0. In Figure I-9 it is apparent that this condition prevails only at low zinc concentrations and either high or low magnesium concentrations. However, at high magnesium concentrations, uranium has a very low solubility, and at low magnesium concentrations the distribution coefficients are highly sensitive to magnesium concentration, leading to process control difficulties. Thus it appears that the magnesium concentration should be between about 20 and 40 a/o and that the zinc concentration should be low. Since the distribution coefficient of praseodymium in this region is somewhat below 2.0, other means of increasing the distribution coefficients, such as variation in temperature and salt composition, are being investigated. The distribution coefficients of uranium and plutonium are sufficiently low that they could also be increased, if necessary, and still be well below the value of 2.0.

Some effects of variations in temperature and salt composition on the distribution coefficients of praseodymium and plutonium between 50 a/o Zn-50 a/o Mg solution and various magnesium chloride-based salts are shown in Figure I-10. The distribution coefficients of plutonium increased with rising temperature and the distribution coefficients of plutonium and praseodymium were both higher when the lighter

Figure I-10

EFFECT OF TEMPERATURE ON THE DISTRIBUTION BEHAVIOR OF PRASEODYMIUM AND PLUTONIUM

Metal Phase: 50 a/o Zn-50 a/o Mg
 Atmosphere: argon
 Crucible: tantalum
 Mixing Rate: 300 rpm

alkali metal chlorides were used in the salt. Therefore, it would be expected that substitution of LiCl-MgCl₂ for NaCl-KCl-MgCl₂, for example, would increase the praseodymium distribution coefficients in Figure I-9 to a more useful level. Decreasing temperature from about 850°C to 625°C had little effect on the distribution behavior of praseodymium in LiCl-MgCl₂, but lowered the value of the distribution coefficient of plutonium, thereby causing a larger praseodymium-plutonium separation factor [$S.F. = K_d(\text{Pr})/K_d(\text{Pu})$]. Earlier work had also shown, as would be expected from the mass action effect in Reaction 1, that increasing the MgCl₂ concentration increases all of the distribution coefficients. An optimum salt mixture should therefore consist of light alkali metal chlorides and a high concentration of MgCl₂, and should have a melting point below 500°C.

During the course of these studies, the distribution behavior of some transuranium elements between magnesium chloride and zinc-magnesium alloy was examined briefly. The results, shown in Figure I-11, suggest that this method may be applicable to the separation of certain transplutonium elements from one another. In general, neptunium, plutonium, and curium distribute strongly to the metal phase, while americium, californium, and einsteinium tend to favor the salt phase. This type of separation would

Figure I-11

DISTRIBUTION OF TRANSURANIUM ELEMENTS BETWEEN MAGNESIUM CHLORIDE AND ZINC-MAGNESIUM ALLOY

Conditions

Temp: 800°C^a
 Mixing Rate: 300 rpm
 Crucible: tantalum^a
 Atmosphere: argon

have the advantages of large separation factors and of using solvents which are resistant to irradiation damage. No concerted process development work has been devoted to this possibility thus far.

c. Liquidus Temperatures of Ternary Salt Systems

In the preceding discussion, the need was mentioned for low-melting salts composed of alkali metal chlorides and high concentrations of MgCl_2 . Liquidus surfaces of the ternary systems LiCl-KCl-MgCl_2 and LiCl-NaCl-MgCl_2 are therefore being determined in the composition regions of interest by thermal analysis techniques. Results that were obtained in the MgCl_2 -rich region of the system LiCl-KCl-MgCl_2 are shown in Figure I-12. These results indicate that a melting point as low as 450°C can be reached at a MgCl_2 concentration of 60 m/o, which should result in sufficiently high distribution coefficients for the rare earths.

d. Solubility of Magnesium Fluoride in the System Calcium Chloride- Magnesium Chloride

During the investigations related to the EBR-II skull reclamation process, indications were obtained that the MgF_2 in the 47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5.0 m/o MgF_2 salt used in the uranium oxide reduction step at 800°C might be near the solubility limit. The studies of molten salts were therefore extended to include a brief investigation of the solubility of MgF_2 in the binary system CaCl_2 - MgCl_2 at temperatures in the range 600 to 800°C. Filtered samples were withdrawn from the saturated salt at various temperatures and were analyzed for fluoride.

^a Einsteinium measurements were made in alumina crucibles at a temperature of 710°C.

Figure I-12

PARTIAL DIAGRAM OF THE LIQUIDUS SURFACE
IN THE SYSTEM LiCl-KCl-MgCl_2

(Tentative)

The results, presented in Table I-3, indicate that at 800°C the MgF_2 is indeed near or at saturation in the above-mentioned salt. The MgF_2 solubility increases from about 5 m/o in the equimolar mixture to values of about 11 and 15 m/o, respectively, in the pure components. The temperature coefficient of MgF_2 solubility appears to be negligible within the accuracy of the results.

e. Solubility of Plutonium in Calcium-Zinc Solutions

A process which has been considered for the separation of rare earth fission products from uranium and plutonium consists of dissolving the fuel in zinc, then adding sufficient calcium to precipitate the uranium and plutonium, leaving the rare earths in solution. Previously reported data on the solubility of uranium in calcium-zinc solutions are combined with more recently determined plutonium solubility results in Figure I-13. The solubility of uranium becomes extremely low at the higher calcium concentrations. Although the solubility of plutonium also decreases with increasing calcium concentration, it appears that the solubility reaches a minimum of about 0.05 to 0.1 w/o. Attempts to decrease the solubility of plutonium below this value by lowering the temperature or increasing the calcium concentration were thwarted by the precipitation of solvent metals.

Table I-3

SOLUBILITY OF MAGNESIUM FLUORIDE IN THE SYSTEM $\text{CaCl}_2\text{-MgCl}_2$

<u>MgCl₂ Conc. (m/o)</u>	<u>MgF₂ Solubility (m/o)^a</u>				
	<u>600°C^b</u>	<u>650 C^b</u>	<u>700°C^b</u>	<u>750°C^b</u>	<u>800°C^b</u>
0					15
10			13.1	14.5	12.5
15			11.6		11.4
30		7.4			
35			4.1		
40		5.4	4.6		
50		4.8	5.0	5.0	
60	6.8	6.3	6.1		
70		5.7	6.0	5.7	
80			7.1	7.3	7.4
90			9.0	8.6	9.0
100			10.7		

^aAverage values are reported.

^bSince the temperature coefficient of MgF_2 solubility is very low, the temperature at which the solubilities are reported is given to the nearest 25°C.

The feasibility of a practical process based on this type of separation appears to be marginal. This approach has therefore been discontinued in favor of the liquid metal-molten salt extraction, which is believed to show greater promise.

f. Processes for Refractory Fuels

Since oxides, carbides, and other compounds of uranium and plutonium are being considered as fast reactor fuels, possible modifications of the conceptual process for metallic fuels (shown in Figure I-6) to accommodate these materials are being investigated. To date, this work has been directed primarily toward carbide fuels.

For a mixed uranium-plutonium oxide fuel, it should be possible to reduce the oxides to produce a magnesium-zinc solution of the metals in the same way that uranium oxide is reduced in the EBR-II skull reclamation process (see Figure I-3). This liquid metal solution would then become the feed to the process shown in Figure I-6.

For a carbide fuel, the carbides could be oxidized and then handled similarly. In addition to oxidation by air or oxygen, recent work

Figure I-13

SOLUBILITIES IN ZINC-CALCIUM SOLUTIONS

carbide fuels. The metallic product of the process should be a suitable material from which new fuel could be made, particularly in the case of carbide fuels. Further work is needed, however, to obtain information on the technical and economic feasibility of such a process.

4. Materials Evaluations

Studies are being made to evaluate various materials for the containment of liquid metal and liquid salt systems of the types contemplated for reprocessing fast reactor fuels. The main objective of the work is the selection of materials and equipment items for EBR-II processes, but information of a more general interest is also being accumulated.

has shown that UC can be oxidized conveniently by NaNO_3 or Na_2CO_3 in a molten salt such as LiCl-MgCl_2 to form uranates, which are readily reducible by magnesium-zinc solutions in the presence of fluxes containing magnesium chloride. It is advantageous in the case of carbides, however, to avoid oxidation, thereby eliminating a relatively large volume of radioactive waste salt necessary to remove MgO that is produced as a by-product of the subsequent uranium oxide reduction step.

Chlorine, hydrogen chloride, and zinc chloride have all proved to be capable of converting UC pellets in a molten chloride solvent to soluble uranium chlorides and free carbon. Although this approach eliminates the problem of MgO formation in the process, it introduces the necessity for handling finely divided solid carbon in the salt. A similar situation occurs when UC is decomposed by liquid zinc to form a uranium-zinc solution and carbon. Studies are currently underway to determine the effect of free carbon on the process and to develop a method of removal if necessary. It appears that a process of this type could, in principle at least, accommodate oxide and

a. Corrosion of Tungsten and Molybdenum-30 Weight Percent Tungsten Alloy in a Zinc-Halide Flux System

Both tungsten and molybdenum-30 w/o tungsten are employed as containment materials for the molten magnesium-zinc alloys and halide flux systems of the skull reclamation and blanket processes. Because the molybdenum-tungsten alloy is machinable, it is used for accessory parts (agitators, transfer lines, etc.) in process equipment. This alloy is brittle at room temperature, although considerably less so than tungsten, and care must be taken in handling fabricated parts. Some breakage has been experienced. The durability of fabricated items has been increased by improved designs and machining methods.

Further corrosion testing of tungsten and a molybdenum-30 w/o tungsten alloy has been carried out in a zinc-halide flux system* employed in a step of the skull reclamation process at a temperature 200°C higher than that used in the process (1000°C instead of 800°C). In a 500-hr test at 1000°C, tungsten was attacked intergranularly to a depth of 2 to 4 mils and the molybdenum-tungsten alloy to a depth of 2 to 8 mils (see Table I-4). Grain sizes were not greatly affected. Sharp edges remained on the specimens, and dimensional changes were less than 1 percent. Virtually no leaching of molybdenum by zinc occurred from the Mo-W coupons. However, in this experiment, leaching of molybdenum was curtailed by rapid saturation of the zinc phase with molybdenum;** molybdenum was leached not only from the coupons, but also from the Mo-W corrosion capsule (see experimental conditions, Table I-4). Therefore, for the Mo-W alloy, it may be concluded only that the rate of attack of the Mo-W alloy by molybdenum-saturated zinc solutions is very low.

Two large pressed-and-sintered tungsten crucibles (13-in. OD by 19 in. high) have been in service in the skull reclamation process pilot plant, one for about a year, the other for about six months. During this time they have been used an average of about two times a week for process operations which range in duration from about eight hours to nearly 48 hours. No visible signs of corrosion of these crucibles are evident. While they have withstood repeated freezing and remelting of salt-and-metal or metal charges, the older of the two large crucibles recently cracked during remelting of a full charge of salt and a 50% magnesium-zinc alloy (crucible was about 60% full). Although this failure is disappointing and indicates that remelting operations should, if possible, be avoided, the crucibles have, nevertheless, performed very well. Several smaller pressed-and-sintered tungsten

*The flux composition employed is given in Table I-4. However, in the flux now used in the skull reclamation process, CaCl_2 is used instead of LiCl . This change should not have a significant effect on corrosion rate.

**Solubility of molybdenum in zinc at 1000°C is about 0.03 w/o.

Table I-4

CORROSION OF TUNGSTEN AND MOLYBDENUM-30 WEIGHT PERCENT
TUNGSTEN ALLOY EXPOSED TO THE SALT-METAL SYSTEM
OF THE NOBLE METAL EXTRACTION STEP OF THE
EBR-II SKULL RECLAMATION PROCESS

Conditions:

Time and Temp.:	500 hr at 1000°C
Metal Phase:	40 g zinc
Flux Phase:	20 g of composition (m/o): 46.6 LiCl, 46.6 MgCl ₂ , 4.8 MgF ₂ , 2.0 ZnCl ₂
Containment:	Mo-30 w/o W welded capsule enclosed in a 310 SS capsule. One capsule containing all six speci- mens was contained in a rocking furnace which was oscillated through 180 degrees at two cycles per minute.
Specimen Size:	0.09 x 0.09 x 1.5 in.

Material	Specimen Thickness		Photomicrograph Results
	Initial (mils)	Change (mils)	
W	90.1	+0.4	{ Occasional 2- to 4-mil cavitation with 2-mil intergranular attack.
W	89.0	-0.7	
W	89.5	-0.5	
Mo-W	86.8	+0.3	{ 2- to 8-mil intergranular attack. No obvious molybdenum leaching.
Mo-W	90.7	-0.3	
Mo-W	90.7	-0.9	

crucibles (4-in. OD by 9 in. high) which have been in similar use for over two years show no signs of corrosion or deterioration.

b. Plasma-Sprayed Tungsten Coatings

Although tungsten possesses excellent resistance to corrosion by the molten zinc-magnesium and halide salt solutions of the EBR-II skull reclamation and blanket processes, large tungsten vessels or complex shapes are difficult to fabricate and, as a result, are expensive. For this reason the feasibility of using plasma-sprayed tungsten

coatings on various substrate materials is being examined. In thermal cycle tests of 3-in.-square coupons (twelve cycles between 300 and 800°C), no deterioration of tungsten-coated silicon carbide (nitride or oxide-bonded), tungsten-coated Alundum, and tungsten-coated type 430 stainless steel was evident. Subsequently, a relatively large silicon carbide crucible (10 1/2-in. OD by 15 in. high) and a type 410 stainless steel crucible (10 1/2-in. OD by 21 in. high) were procured, and the interior surfaces were plasma-sprayed with tungsten. These withstood, without evident damage, four thermal cycles between 900°C and 300°C and four between 900°C and room temperature. However, when the stainless steel crucible was subsequently used to contain a charge of 50 w/o magnesium-zinc alloy, the tungsten coating cracked and peeled. The tungsten-coated silicon carbide crucible was used to contain several zinc-magnesium alloys and one charge of salt flux at 800°C without indication of deleterious effect on the tungsten coating, but a large horizontal crack developed in the crucible about halfway up the wall after the crucible had been exposed to air for about one week. The crack is believed to have been caused by penetration of the salt flux into the pores of the crucible (indicating imperfections in the tungsten coating) and subsequent expansion of the salt as it absorbed water from the room air. However, for inert atmosphere service, tungsten-coated silicon carbide crucibles show promise; testing of these crucibles will continue.

c. Beryllia Crucibles

In the EBR-II skull reclamation process a beryllia crucible is required for the final uranium retorting step. Beryllia has the very desirable characteristic of not reacting significantly with the solvent metals, magnesium and zinc, or with molten uranium, the product of the retorting operation. In work to date, beryllia has also had the desirable property of being unwetted by molten uranium -- a factor which could influence which method is chosen for removal of the retorted uranium product (e.g., pouring or physical removal as a solidified mass). The required size of the beryllia retorting crucible is about 8-in. OD by 15 in. high, which is considerably smaller than that of the beryllia crucible previously considered for the uranium precipitation steps of the skull reclamation process. Satisfactory beryllia or beryllia-lined crucibles for retorting have not yet been procured. Isopressed beryllia crucibles were used in initial retorting operations but were subject to cracking. Alternative procedures of manufacturing full-scale crucibles are being investigated. These include thixotropic casting and flame deposition of beryllia linings on other ceramic crucibles, such as silicon carbide or Alundum.

Plasma-spraying of beryllia on Alundum, silicon carbides, or tungsten is also being investigated. Beryllia-coated Alundum coupons were unaffected by twelve thermocycles between 300°C and 800°C. Full-size beryllia-coated Alundum crucibles are presently being obtained for tests. Evaluation of beryllia coatings plasma-sprayed on tungsten and silicon carbide is in progress.

d. Stability of Solutions of Uranium in Molten Magnesium-Zinc Alloys

Several experiments were made at 800°C to determine the effects of small amounts of added impurities on the stability of solutions of uranium in 5 w/o magnesium-zinc. Neither beryllium added to 0.05 w/o, which is slightly in excess of its solubility value, nor aluminum added to 1 w/o had an effect on uranium concentrations. Silicon caused direct precipitation of the uranium. Stainless steel dissolution had no effect up to a concentration of 0.1 percent, but at a concentration of 1 percent caused a slight but perceptible (less than 5 percent) decrease in uranium concentration. This decrease in uranium concentration is believed to have been caused by reaction with elements, such as carbon or silicon, which are present at low concentrations in stainless steel.

e. Containment of Molten Uranium in Tungsten or Tantalum

Various materials are being evaluated in a search for new and better materials for containing molten uranium and its alloys at elevated temperatures (to as high as 3000°C for possible use in advanced reactors). The first two materials to be evaluated were tungsten and tantalum. At below-saturation concentrations, uranium at 1200°C corroded tungsten rapidly by a simple solution mechanism. Attack of tungsten by a uranium-iron alloy was also extensive at 900°C. Tantalum rods in molten uranium at 1200°C were apparently penetrated by the uranium, since extensive swelling of the rods occurred. It is concluded that neither tungsten nor tantalum is a good container material for molten uranium.

5. Supporting Engineering Studies

Engineering studies of liquid metal systems are in progress in the areas of mass transfer, heat transfer, mixing, liquid metal boiling, and determination of critical constants of alkali metals.

a. Mass Transfer in Flowing Metal System

A study of the mass transfer of uranium to flowing cadmium at Reynolds numbers up to 5×10^5 has been completed (see ANL-6766, pp. 36-38). This study was the subject of a PhD thesis by a research associate from Ohio State University. The rate of mass transfer from 1/2-in. diameter uranium spheres (one sphere used in each run) to cadmium flowing around the spheres in a 1 1/2-in. Type 304 stainless steel pipe was investigated as a function of flow rate and prior metallurgical treatment of the uranium. A pronounced "hump" in the curve of mass transfer factor, J_d (a dimensionless group which includes the mass transfer coefficient and the physical properties of the cadmium solvent), occurred at Reynolds numbers of about 7×10^4 (see Figure I-14). Mass transfer rates were

Figure I-14

CORRELATION OF DATA FOR MASS TRANSFER FROM URANIUM SPHERES TO FLOWING CADMIUM

strongly affected by previous metallurgical treatments. Uranium spheres which had been quenched from the beta phase region (667 to 775°C) to produce fine, randomly oriented grains dissolved more rapidly than spheres with coarse grains having a preferred orientation.

b. Mixing of Liquid Metal-Salt Systems

Whenever time has been available, a dynamometer has been employed to determine quantitatively the effect of agitation on the rates of various reactions occurring between liquid metal and salt phases, e.g., reduction of uranium or thorium oxide in liquid metal-salt systems. That agitation is an important variable in these reactions is shown in Figure I-15, where the rate of reduction of uranium oxides suspended in a molten salt by a magnesium-zinc alloy is plotted as a function of mixing power input to the system. Since this reduction reaction is required in the EBR-II skull reclamation process (see Figure I-3), oxidized melt refining crucible residues (skulls) were used in this investigation. The skull oxides employed consisted predominantly of uranium oxides together with oxides of the noble fission product elements. Similar data will be obtained on the effect of agitation on the rate of reduction of thorium and the rate of extraction of noble metals in the noble metal extraction step of the skull reclamation process. In connection with the mixing studies, photographs were taken of mixing patterns produced in immiscible phases of widely different densities (a liquid metal having a density of 8 g/cc and water) as a function of agitator shape, location (with respect to the liquid-liquid interface), and speed. For a particular agitator speed, the greatest dispersion of the phases in each other was obtained with an upward-deflecting agitator located just below the metal-salt interface.

Figure I-15

EFFECT OF MIXING POWER INPUT ON RATE OF REDUCTION OF URANIUM OXIDES IN A HALIDE FLUX-METAL SYSTEM

- Conditions: 194 g of uranium oxides produced by oxidation of melt refining skulls were suspended in 940 g halide flux (see Fig. I-3) and reduced at 800°C by contacting with 3740 g 5 w/o Mg-Zn alloy.
- Crucible: Tungsten, 4 1/4-in. inside diameter x 9 1/2 in. deep, equipped with four 5/8-in. baffles.
- Stirrer: Tungsten-molybdenum, 2-in. diameter x 5/8-in. height, pitched 30 degrees from horizontal, deflecting downward.

c. Liquid Metal Boiling Studies

Evaporation or distillation of volatile metal solvents is an operation in the liquid metal processes under development for the recovery of nuclear reactor fuels. Consequently, this operation has received considerable attention over the past several years.

(1) Performance of Large-Scale Cadmium Distillation Unit

A large-scale cadmium distillation unit (capable of distillation rates of up to 100 kg/hr) has been operated intermittently over the last several years as part of a program to develop engineering technology for the metal distillation or evaporation steps present in nearly all liquid metal processes for recovery of nuclear fuels. During the past year, work with the large-scale cadmium distillation unit was completed. In the final series of runs, a de-entrainment device which had been installed in the vapor space of the still pot reduced the entrainment of liquid cadmium drops in the cadmium vapor stream to satisfactory levels (from several percent in the absence of the de-entrainment device to as little as 0.9% with the device). An eddy-current induction probe (see Skull Reclamation

Process) was also used in these runs to measure continuously the cadmium level in the still pot. This instrument gave promise of being effective and accurate for monitoring the metal liquid level in a remotely operated distillation unit. Measurement of the temperature distribution along the vertical axis of the cadmium pool indicated that boiling probably takes place only within the upper inch of the liquid cadmium pool.

(2) Nonturbulent Vaporization of Mercury

The study of nonturbulent vaporization* of mercury was continued. Reasonably high nonturbulent vaporization rates can be expected for liquid metals because of their favorable physical properties such as high density, high thermal conductivity, and high surface tension. In further studies of the nonturbulent vaporization of mercury, it was found that a steep and constant temperature gradient exists in a thin surface liquid layer (about 0.2 in. thick). The largest value of this gradient measured to date is 115°C/in. (see Table I-5). Below this thin surface layer, the pool temperature was almost constant with depth. The vaporizing liquid surface was superheated at an average of 30°C above the vapor space saturation temperature.

d. Determination of Critical Constants of Alkali Metals

A program has been started to determine the critical constants of alkali metals. Densities of the vapor and liquid phases of an alkali metal containing a radioactive isotope will be measured from room temperature up to its critical point by measurements of the gamma radiation emanating from the vapor and liquid regions of the alkali metal held within a small capsule. As the critical point is approached, the densities and therefore the gamma activities emanating from the vapor and liquid phase regions will approach each other.

6. Chemistry of Molten Salts

Since molten salts, as well as liquid metals, are being utilized in various pyrometallurgical processes, fundamental studies of molten chlorides are being conducted to provide supporting data for process use and to gain an understanding of the chemistry involved in the process. Reactions of uranium oxides in molten chloride solvents are of particular interest, since a chloride flux is currently used in the EBR-II skull reclamation process and may have further application for oxide or carbide reactor fuel processing.

Table I-5

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

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

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

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

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

^cThe average thickness of layers having these gradients was 0.17 in.

a. Thermal Decomposition of Uranyl Chloride

Previous work had shown that a soluble uranium (V) species, UO_2Cl , was formed upon the addition of UO_3 , U_3O_8 or UO_2Cl_2 to molten chloride solvents (see ANL-6766, page 47). In the case of UO_2Cl_2 , the UO_2Cl appeared to be formed directly by the thermal decomposition reaction at temperatures above 600°C .

By measuring the amount of chlorine released by this reaction and determining the corresponding increase in optical absorbance of the UO_2Cl in the salt solution, it has been possible to obtain molar absorptivity values for the UO_2Cl spectrum. In the wavelength region where this spectrum occurs, the absorbance of the undecomposed UO_2Cl_2 is negligible.

Once the molar absorptivity values for UO_2Cl had been established, it was possible to determine equilibrium constants for Reaction 1 by simultaneous measurement of the UO_2Cl absorbance and the pressure of chlorine in equilibrium with the salt solution. Values for the equilibrium constant

$$K_{\text{eq}} = \frac{[\text{UO}_2\text{Cl}]^2 [\text{P}_{\text{Cl}_2} \text{ (atm)}]}{[\text{UO}_2\text{Cl}_2]^2}$$

in LiCl-KCl at 650°C are listed in Table I-6.

Table I-6

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

Run	Molar Concentration		Cl_2 Pressure (atm.)	K_{eq} (atm.)
	UO_2Cl_2	UO_2Cl		
159-3	0.143	0.0041	2.6×10^{-3}	2.1×10^{-6}
160-4	0.158	0.0023	2.6×10^{-3}	5.6×10^{-7}
160-5	0.158	0.0017	1.7×10^{-2}	1.9×10^{-6}
163-1	0.179	0.0183	1.6×10^{-4}	1.7×10^{-6}
163-2	0.172	0.0247	4.0×10^{-5}	8.2×10^{-7}
163-3	0.195	0.0023	9.9×10^{-3}	1.4×10^{-6}
164-1	0.138	0.0108	1.2×10^{-4}	7.3×10^{-7}
164-3	0.133	0.0161	4.0×10^{-5}	5.9×10^{-7}
				Av. 1.2×10^{-6}
				Standard Deviation = 0.6×10^{-6}

When molten chloride solutions of UO_2Cl and UO_2Cl_2 were held under vacuum for several hours at temperatures above 750°C , a second thermal decomposition reaction was observed:

This reaction was characterized by the precipitation of black UO_2 , which was separated from the salt by filtration and identified by X-ray diffraction. By working at temperatures below 750°C , it was possible to avoid Reaction 2 during the investigations of UO_2Cl .

The results of this work indicate that Reaction 1 represents the initial step in the thermal decomposition of UO_2Cl_2 in molten chloride solvents. The reaction is easily reversible and reaches a measurable equilibrium at 600 to 650°C . At temperatures above 750°C , further decomposition of UO_2Cl to UO_2 and chlorine takes place, as shown by Reaction 2. Evidence that Reactions 1 and 2 are both reversible is provided by the fact that UO_2 suspended in a molten chloride solvent can be converted to UO_2Cl_2 by passing chlorine through the mixture.

b. Effects of Solvent and Temperature on the UO_2Cl Spectrum

In most of the experimental work on the UO_2Cl spectrum, either the LiCl-KCl eutectic or the NaCl-KCl-MgCl_2 eutectic was used as the solvent. The effect of changing temperature on the UO_2Cl spectrum in the ternary eutectic solvent is illustrated in Figure I-16. In this, as well as other solvents that were investigated, the UO_2Cl spectrum was influenced at the shorter wavelengths by the absorption spectrum of UO_2Cl_2 in equilibrium with the UO_2Cl , and by a shift of the charge-transfer absorption edge to longer wavelengths with increasing temperature.

Figure I-16

URANYL (V) SPECTRUM IN NaCl-KCl-MgCl_2 EUTECTIC

Data on the effect of solvent composition on the UO_2Cl spectrum are summarized in Table I-7. It is generally agreed that the linear O-U-O group gives rise to the spectra of uranyl (V) and (VI) compounds. Changes in the composition of the molten salt solvent are believed to cause differences in the attractions between the solvent cations and the oxygen atoms in the O-U-O group, with the result that the O-U bond lengths are altered, producing differences in the splitting of the energy levels which are reflected in the spectrum.

Table I-7

ABSORPTION MAXIMA OF UO_2^{2+} IN DIFFERENT SALTS AT 650 C

<u>Solvent</u>	<u>Wavelength, λ_{max} mμ</u>						
59 m/o LiCl-41 m/o KCl (eutectic)	625	800	1535	1610	1665	(1925) ^a	
50 m/o LiCl-35 m/o KCl-15 m/o MgCl ₂	660	825	1525	1610	1660		
50 m/o LiCl-50 m/o MgCl ₂	670	855	1520	1610	1660	1930	
100 m/o MgCl ₂ ^b	670	855	1515	1615	1660	1930	
30 m/o NaCl-20 m/o KCl-50 m/o MgCl ₂ (eutectic)	685	860	1520	1615	1660	1930	

^aUncertain.^b750°C.

The basic chemical reactions of uranium oxides with the molten chlorides that are used in the present processes apparently are reasonably well understood, and no further work on this subject is planned at present.

C. Chemistry of Liquid Metals

The chemistry of liquid metal systems is being investigated to provide basic concepts and data for the design of methods for the processing of nuclear materials and to provide a basis for the development of liquid alkali metal technology. In addition, these studies are contributing to our understanding of liquid metal solutions.

1. Phase Studies

Metallic solutions are used in all of the pyrometallurgical processes being developed. Therefore, it is necessary to know the solid-liquid phase relations of a large number of binary, ternary, and multicomponent metallic systems. Solubility measurements have been used to determine the liquidus for the majority of systems of practical importance. The solid phases in equilibrium with the saturated solutions have been determined by the use of conventional metallurgical methods, i.e., by either isolation or synthesis, followed by chemical analysis and X-ray diffraction characterization. Thermal analyses have supplemented the other methods in some instances. In addition, a method involving the use of the continuous recording effusion balance in combination with X-ray identification has been

developed into a powerful technique for the elucidation of very complex phase diagrams.

a. The Technetium-Zinc System

The Tc^{99} -Zn system has been studied by thermal, metallographic, X-ray, sampling, and effusion techniques. Figure I-17 shows the diagram constructed from the experimental results. The system contains two intermediate phases: TcZn_6 and a more zinc-rich phase, "U" phase, which has not been completely characterized. Diffraction patterns of TcZn_6 can be indexed on the basis of a face-centered cubic cell with $a_0 = 7.588 \pm 0.001 \text{ \AA}$. The "U" phase was found to have a zinc-to-technetium atom ratio between 15 and 18.

Figure I-17

TECHNETIUM-ZINC PHASE DIAGRAM

The liquidus line in Figure I-17 was determined by chemical analysis of filtered samples taken from the saturated melt. The solubilities are given as functions of temperature, in degrees Kelvin, by Equations 1 and 2:

$$(470 \text{ to } 544^\circ\text{C}) \log (a/o \text{ Tc}) = 6.431 - 7159 T^{-1}, \quad (1)$$

$$(544 \text{ to } 758^\circ\text{C}) \log (a/o \text{ Tc}) = 9.413 - 15690 T^{-1} - 4.979 \times 10^6 T^{-2}. \quad (2)$$

The break in the liquidus at 544 C is in good agreement with differential thermal analysis arrests observed at 542°C (8 w/o Tc alloy) and 554°C (13 w/o Tc alloy). Another arrest was observed at about 950°C. The equilibria involved are:

No evidence was found for the formation of solid solutions in the terminal phases.

b. The Plutonium-Cadmium System

Preliminary measurements of the solubility of plutonium in cadmium (ANL-5959) indicated a break in the liquidus curve at about 400°C, which could be attributed to a peritectic reaction in the system. To supplement our thermodynamic studies of this system, the solid phases in the cadmium-rich portion of the diagram have been characterized.

To prepare the solid phase that is in equilibrium with the saturated liquid below 400°C, plutonium was slowly electrolyzed into a pool of cadmium (99.95%) at about 380 C. The anode was high-purity plutonium metal (10 ppm Fe, 2 ppm Ni, 1 ppm Cr); the electrolyte was PuCl_3 (0.29 w/o) dissolved in LiCl-KCl eutectic. The resultant alloy electrode contained an intermetallic phase which was shown by X-ray examination to have a structure similar to UCd_{11} . The intermetallic compound, PuCd_{11} , continuously precipitated in the cadmium pool as plutonium was added by electrolysis; when the alloy was cooled, additional PuCd_{11} precipitated.

A mossy crystalline growth surmounting the alloy phase was observed in the sample prepared by electrolysis. The X-ray patterns of this material were not satisfactory but indicated that it may be another, more plutonium-rich phase.

To prepare the solid phase that is in equilibrium with the saturated liquid above 400°C , a mixture with a plutonium to cadmium ratio of 7 to 1 was heated to 650°C for several hours and then annealed at 600°C for two weeks. Metallographic examination of the quenched alloy indicated some unalloyed cadmium and an intermetallic phase; the intermetallic phase had an X-ray diffraction pattern similar to that observed for the rare earth-cadmium compounds of the MCd_6 type.

The solubility of plutonium in liquid cadmium was redetermined over the temperature range $335\text{--}632^{\circ}\text{C}$. Figure I-18 shows the solubility data obtained. The saturating phase below 399°C is PuCd_{11} ; the solid phase in equilibrium with the solutions above the peritectic is PuCd_6 .

c. Solubility of Argon and Krypton in Liquid Sodium

An investigation of the solubility of rare gases in liquid alkali metals is underway. The data will be used to gain a better understanding of the factors important in determining solubilities in liquid metals. The rare gases are expected to dissolve in liquid metals as unexcited atoms, since the promotional energy to the p^5 configuration is very large (ranging from 156 kcal/mole for radon to 383 kcal/mole for neon). The electrons of the rare gas atoms will therefore not be available for metallic binding and the principal interaction will be between neutral rare gas atoms and metal ions. The energetics of this interaction can be estimated from the temperature coefficient of the solubility.

Figure I-18

SOLUBILITY OF PLUTONIUM IN LIQUID CADMIUM

excited atoms, since the promotional energy to the p^5 configuration is very large (ranging from 156 kcal/mole for radon to 383 kcal/mole for neon). The electrons of the rare gas atoms will therefore not be available for metallic binding and the principal interaction will be between neutral rare gas atoms and metal ions. The energetics of this interaction can be estimated from the temperature coefficient of the solubility.

The experimental procedure for determining the solubility of argon and krypton in liquid sodium consists of four steps:

(1) About three liters of liquid sodium is saturated with rare gas (either radioactive krypton of known specific activity or argon) by circulation of the gas through the

liquid metal for a period of about three hours at each selected temperature. After saturation, the liquid metal is allowed to stand at the given temperature and pressure for several hours to free the solution of entrapped gas bubbles.

(2) One-third to two-thirds of the saturated metal is transferred to a second vessel where the dissolved rare gas is removed by sparging. (In the case of the argon experiments, the sparging gas was helium. In the case of the krypton studies, the sparging gas was helium to which a known amount of inactive krypton had been added. The sparging in both cases was carried out at one atmosphere pressure.)

(3) The helium which now contains the rare gas is circulated through a liquid nitrogen-cooled charcoal trap, where the rare gas and some helium is adsorbed from the gas stream.

(4) In the case of the argon experiments, the trap is first pumped out to about 35 mm of pressure to remove most of the helium and is then heated to about 390°C to desorb the rare gas. A known portion of the desorbed gas is removed and analyzed for argon by means of a mass spectrometer.

In the case of krypton, the trap is pumped out to less than one micron pressure to remove the helium completely. The krypton is then desorbed by heating the trap, and the amount of krypton dissolved in the sodium is calculated from the specific activity of the desorbed gas.

Figure I-19

HENRY'S LAW PLOT OF THE SOLUBILITY OF ARGON IN SODIUM AT 480°C

The solubility of argon in liquid sodium was measured as a function of pressure at 480°C. The solubility was found to be proportional to the pressure (Figure I-19) and hence Henry's law applies to these solutions.

The solubilities of argon and krypton at one atmosphere in liquid sodium are shown as a function of temperature in Figure I-20. These data may be represented by the equations:

$$\text{Ar: (340-480°C) } \log (\text{atom fraction}) = -3.867 - 3533 T^{-1}$$

$$\text{Kr: (200-480°C) } \log (\text{atom fraction}) = -4.188 - 3583 T^{-1}$$

The heats of solution computed from these data are 16.2 kcal/mole for argon and 16.4 kcal/mole for krypton.

Figure I-20

TEMPERATURE DEPENDENCE OF THE SOLUBILITY OF RARE GASES AT ONE ATMOSPHERE IN SODIUM

2. Thermodynamic Studies

Thermodynamic functions are being determined for metallic systems that are of importance to pyrometallurgical processes and for systems where knowledge of the thermodynamics will be particularly useful for the testing of theories of metallic solutions. Three methods are being used:

1. High temperature galvanic cells are especially useful for the measurement of activities in liquid metal solutions, as well as for the determination of the free energy of formation of the equilibrium solid phase in solid-liquid two-phase alloys.

2. For systems composed of several well-defined intermetallic phases, measurement of the decomposition pressure by the Knudsen effusion method is proving to be most useful.

3. For systems in which only a small difference in electrochemical potential of the components exists and in which both components have appreciable vapor pressures, a vapor phase optical absorption method is being developed.

a. Thermodynamic Properties of TcZn₆

The Tc-Zn system is known to have two intermediate phases: a zinc-rich phase which contains approximately 5.5 a/o technetium

Table I-8

DECOMPOSITION PRESSURE AND STANDARD FREE ENERGY OF
FORMATION OF TcZn_6

Temp. (°C)	P_{mm} (obs.)	$-\Delta G_f^\circ$ (kcal/g-atom)
470.0	0.0592	3.02
480.0	0.0778	3.03
488.4	0.110	2.89
500.0	0.156	2.85
510.0	0.203	2.86
520.0	0.299	2.68
530.0	0.366	2.75
541.7	0.594	2.47
552.4	0.789	2.43
560.0	0.914	2.46
570.0	1.114	2.50

Figure I-21

DECOMPOSITION PRESSURE
OF TcZn_6

and a technetium-rich phase which corresponds to the formula TcZn_6 . The standard free energy of formation of this latter compound has been determined by measuring the vapor pressures of zinc in the equilibria

over the temperature range of 470 to 570°C. Vapor pressures were measured by means of a recording effusion balance.

The observed decomposition pressures of TcZn_6 are listed in column 3 of Table I-8 and are graphically shown in Figure I-21. The data may be represented by the empirical equation

$$\log P_{\text{mm}} = 9.853 - 8242 T^{-1}$$

(± 0.024 std. dev.)

The standard free energy of formation values for TcZn_6 , listed in column 4 of Table I-8, were computed by means of the relation ΔG_f° (cal/g-atom) = $x_{\text{Zn}} RT \ln (P/P^\circ)$, in which x_{Zn} is the atom fraction of

zinc (6/7) in the compound, P is the decomposition pressure of the alloy at temperature T , and P° is the vapor pressure of pure liquid zinc. Values of P° were calculated using the equation given by Barrow⁴ and his coworkers. The free energy may be represented by the empirical equation

$$\Delta G_f^\circ (\text{cal/g-atom}) = -7823 + 6.43 T (\pm 75 \text{ std. dev.})$$

Thermal analysis studies have indicated that TcZn_6 decomposes peritectically into pure technetium metal and a saturated liquid zinc solution at about 950°C . Extrapolation of the above equation indicates that $\Delta G_f^\circ = 0$ at 944°C ; in view of the long extrapolation, this is in satisfactory agreement with the thermal analysis result.

The partial molal excess free energy of technetium in saturated solutions, $\bar{G}^{\text{xs}}$, may be computed from the free energy of formation of TcZn_6 and the solubility of technetium in liquid zinc. At 500°C , $\bar{G}^{\text{xs}} = -3.2 \text{ kcal/g-atom technetium}$, indicating that technetium in zinc shows only a moderate negative deviation from ideal solution behavior. The low solubility of technetium in liquid zinc (6×10^{-3} a/o at 500°C) is therefore due to the great stability of TcZn_6 ($\Delta G_f^\circ = -20.0 \text{ kcal/mole}$ at 500°C) rather than a large positive deviation from ideality.

b. Thermodynamic Study of the Pu-Cd System

The thermodynamic properties of plutonium in liquid cadmium solutions were determined using high temperature galvanic cells similar to those used with the plutonium-zinc system (ANL-6766, p. 53). Two cells were operated; cell 1 contained 0.29 w/o PuCl_3 in molten LiCl-KCl eutectic and cell 2 contained 2.3 w/o PuCl_3 . Data were obtained for saturated and unsaturated solutions of plutonium in liquid cadmium. The difference in PuCl_3 concentrations did not affect the emfs of the cells, as may be seen in Figure I-22, where the emfs of the two cells are shown as a function of cell temperature. The cell reaction below 413°C when the alloy compartment contained saturated solutions is:

above 413°C , the corresponding reaction is:

The free energies of formation for the PuCd_x intermetallics were calculated from the saturated emf data using the equation:

$$\Delta G_{\text{PuCd}_x}^\circ = -3FE + XRT \ln a_{\text{Cd}}.$$

⁴Barrow, R. F., et al., Trans. Faraday Soc., 51, 1354 (1955).

Figure I-22

EMF OF Pu-Cd GALVANIC CELLS VERSUS TEMPERATURE

The activity of cadmium was calculated from the unsaturated solution data by means of the Gibbs-Duhem equation. The free energies of formation of the intermetallics are:

(693-904°K)

$$\Delta G_{\text{PuCd}_6}^{\circ} \text{ (kcal/mole)} = -13.61 - 38.75 \times 10^{-3} T + 40.43 \times 10^{-6} T^2;$$

(631-682°K)

$$\Delta G_{\text{PuCd}_{11}}^{\circ} \text{ (kcal/mole)} = -45.92 + 35.69 \times 10^{-3} T.$$

The unsaturated solution data were used to compute the excess free energy of plutonium, $\bar{G}_{\text{Pu}}^{\text{xs}}$, in liquid cadmium solution (reference state - pure solid plutonium). These data are fitted by the empirical equation:

(634-904°K)

$$\frac{\bar{G}_{\text{Pu}}^{\text{xs}}}{(1-N_{\text{Pu}})^2} \text{ (kcal/g-atom)} = (-33.74 - 3172 N_{\text{Pu}}) + (23.00 - 6647 N_{\text{Pu}}) \\ \times 10^{-3} T + (2.560 + 3458 N_{\text{Pu}}) \times 10^{-6} T^2.$$

From this equation, one obtains:

$$\frac{\bar{S}_{\text{Pu}}^{\text{xs}}}{(1-N_{\text{Pu}})^2} (\text{cal/degree g-atom}) = (-23.00 + 6647 N_{\text{Pu}}) - (5.119 + 6917 N_{\text{Pu}}) \times 10^{-3} T,$$

$$\frac{\bar{L}_{\text{Pu}}}{(1-N_{\text{Pu}})^2} (\text{kcal/g-atom}) = (-33.74 + 3172 N_{\text{Pu}}) - (2.560 + 3458 N_{\text{Pu}}) \times 10^{-6} T^2.$$

The dependence of the excess quantities on the temperature and the mole fraction of plutonium in solution, N_{Pu} , is shown by the equations. Table I-9 shows a comparison of the excess quantities at 450°C for plutonium at infinite dilution in molten zinc and cadmium solutions.

Table I-9

EXCESS THERMODYNAMIC FUNCTIONS FOR PLUTONIUM
AT 450°C AT INFINITE DILUTION

Solvent	$\bar{L}_{\text{Pu}}$ (kcal/g-atom)	$\bar{S}_{\text{Pu}}^{\text{xs}}$ (cal/degree g-atom)
Cd	-36	-27
Zn	-45	-25

c. Thermodynamics of the Lanthanum-Cadmium System

Five intermetallic compounds are known to exist in the system lanthanum-cadmium: LaCd_{11} , $\text{La}_2\text{Cd}_{17}$, $\text{La}_3\text{Cd}_{13}$, LaCd_2 , and LaCd . Decomposition pressures over alloy mixtures comprised of neighboring pairs of the phases were measured by means of the recording effusion balance.

The Clausius-Clapeyron plot of the decomposition data shown in Figure I-23 also includes the known vapor pressure of liquid cadmium.⁵ The decomposition pressures in the LaCd - La region were estimated from these data and emf data.

d. Thermodynamics of Binary Alkali Metal Solutions

Development of a workable theory of metallic solutions has been slow. The electron theory of metals, formulated some 30 years ago, is still the mainstay of workers in this field. While this theory has had

⁵A. N. Nesmeyanov, Vapor Pressures of Elements, Academic Press, New York, 1963

Figure I-23

DECOMPOSITION PRESSURES OF INTERMEDIATE PHASES IN THE LANTHANUM-CADMIUM SYSTEM

some success in the description of certain physicochemical properties of simple metals (e.g., sodium), it fails to provide a clear understanding of the properties of even the simplest binary metallic solutions. Recognition of this deficiency has aroused recent interest in the potential use of many-body theory^{6,7} in the formation of a more adequate theory of metallic solutions. The need for experimental data to test newly developed theory will soon be felt. It is quite likely that the binary alkali metal solutions, which from the viewpoint of the electronic configuration of partner atoms constitute simple types of solution, will play an important role in this test. A study designed to measure the thermodynamic properties of selected binary liquid alloys formed by the alkali metals was undertaken in this connection.

The high chemical reactivity and chemical similarity of the alkali metals limit the possible experimental methods which may be used to determine thermodynamic activity.

Where multiple species exist in a vapor phase, as in the case of the alkali metals, a vapor pressure method may be used provided that it is possible to determine the partial pressures of the different species independently. With the optical absorption method used in this study, the concentration of atoms of a given alkali metal in the vapor may be distinguished from that of the molecules. Also, the partial pressures of the alkali atoms over a binary alloy may be determined by measuring the light of a certain characteristic frequency (resonance radiation) absorbed by the vapor. Comparison of the absorption by vapor over the alloy with that over the pure metal is a direct measure of the thermodynamic activity of one of the components in the binary solution.

⁶A. Bellemans and M. DeLeener, Phys. Rev. Letters 6, 603 (1961);
Phys. Letters 4, 157 (1963).

⁷H. M. Feder, Argonne National Laboratory, work in progress.

The sodium-potassium system will be the first binary system to be studied. In order to test the absorption technique and the associated apparatus to be used in this study, the enthalpy of vaporization for sodium was determined. The absorption of the 5890 Å line of the sodium doublet by the vapor over pure liquid sodium was measured from 127.7 to 152.7°C. The results are plotted as $\log [T \log I_0/I]$ against $1/T$ in Figure I-24. The quantity $[T \log I_0/I]$ is proportional to the partial pressure of sodium atoms in the vapor over liquid sodium. The

Figure I-24

CLAUSIUS-CLAPEYRON PLOT OF ATOMIC SODIUM IN VAPOR ABOVE PURE LIQUID Na

a. Sodium Purification

One of the principal requirements of the experimental program is a supply of high-purity sodium. One use of such a material is as an aid in the development of the methods for the analysis of sodium for carbon and oxygen in the parts per million range. High-purity sodium is also required for experiments designed to examine the various reactions of liquid sodium. Three processes for the preparation of high-purity sodium have been examined.

The enthalpy of vaporization for the reaction $\text{Na(l)} \rightleftharpoons \text{Na(g)}$ calculated from the temperature dependence of absorption is 25.6 kcal/g-atom at 150°C. The best literature value for this enthalpy⁸ is 24.9 kcal/g-atom at 150°C.

3. Chemistry of Alkali Metals

The utilization of liquid alkali metals as heat transfer media in high power density fast reactors as well as in other power sources makes essential a continuing advancement in alkali metal technology. To insure a sound technological advance, a fundamental research program is needed. A basic program is underway to elucidate the chemistry of reactions that occur in liquid alkali metal solutions; special emphasis will be given to liquid sodium, since its practical importance is presently greatest.

⁸M. Sittig, Sodium, Its Manufacture, Properties and Uses, Reinhold Publishing Corp., New York, N. Y., 1956.

To produce sodium free of oxide, carbon, and heavy metal impurities, a distillation apparatus has been constructed. This is capable of distilling, under vacuum, several pounds of sodium per loading. The distilled sodium, which is collected in a demountable receiver, can be transferred to a helium-atmosphere dry box without exposure of the sodium to air. This avoids the contamination of sodium with oxide.

Trace impurities of carbon and oxygen have been removed from sodium by "gettering" the metal at high temperatures (650 C) for extended periods of time with zirconium metal turnings. This material is then filtered to remove the zirconium turnings. Preliminary analyses for carbon have indicated that this method is effective in reducing the carbon content to low levels (~25 ppm). As yet, no oxygen analysis has been performed on this material.

A third method of producing pure sodium has been to decompose sodium azide. This compound decomposes at 300 C to sodium and nitrogen with no side reactions. The small amounts of metal that have been produced by this reaction have been used to aid in the development of the analytical method for determining carbon in sodium.

b. Solubility of Carbon in Liquid Sodium

It has been established that various metals can be significantly carburized or decarburized when in contact with liquid sodium. This presents a potentially serious problem associated with the use of liquid sodium in nuclear reactors, since undesirable changes in the mechanical properties of a container material, such as steel, may result from small changes in the carbon content of the container material.

Since the mechanism of carbon transport is not understood, a basic study of the transport of carbon in liquid sodium has been started. The initial experiment will be the determination of the solubility of graphite in liquid sodium as a function of both temperature and oxygen content.

c. Carbon Analysis of Sodium

The solubility and carburization studies that are planned will require a reliable method for analyzing sodium for its carbon content. Several analytical techniques for the determination of elemental carbon in sodium are described in the literature.^{9,10} The principle of the existing techniques is the oxidation of carbon to carbon dioxide and subsequent measurement of the quantity of evolved gas. The differences in these

⁹ Pepkowitz, L. D. and Porter, J. T., KAPL-1444, Nov. 1955.

¹⁰ Herrington, J., AWRE, 0 - 62/62

techniques are in the methods of oxidation and in the measurement of the evolved gas. The oxidation of carbon is generally carried out by either direct combustion with oxygen or with a strong oxidizing agent, such as Van Slyke reagent. The available techniques were recently tested,¹¹ but the highly scattered results did not permit comparison of the analytical methods. The discrepancies in the data could equally well have been attributed to sampling and sample preparation techniques.

In the light of the uncertainties, it was necessary to pursue more reliable analytical and sampling techniques. The analytical method chosen for development was the so-called dry oxidation method. In this method, the sodium is first burned under oxygen at low pressure, and then the residue is heated in a silica boat to 1100°C in a stream of purified oxygen at atmospheric pressure. The carbon dioxide produced by the oxidation of the carbon in the sample is collected in a cold trap (maintained at -180°C using liquid oxygen coolant) and subsequently is measured manometrically. Low carbon contents (3-4 μg) were obtained in blank runs. Quantitative recoveries of carbon in standard samples have been obtained (see Table I-10).

Table I-10

RECOVERY OF DIFFERENT FORMS OF CARBON
BY THE DRY OXIDATION METHOD

Form of Carbon	Carbon Added (μg)	Carbon Found (μg)
Sucrose	82.0	85.0
Sodium Carbonate	56.6	56.5
Sodium Carbonate	10.3	10.7
Graphite	44.5	46.0
Graphite	12.2	13.0

Samples of sodium taken from a single solid piece were found to have different carbon contents. It appears that segregation of carbon occurs readily during freezing of the liquid. It was observed, however, that sampling variations can be minimized by sampling from the liquid phase. When this sampling technique was used, an approximately linear relation was obtained between the carbon contents found and the weights of samples taken from a single source of liquid sodium containing 76 ppm carbon. Experiments are now in progress to determine the recovery of carbon as carbonate and graphite from sodium of known carbon content.

¹¹Lockhart, R. W. and Sabol, W. W., GE-APED, Results of the First Round Robin Analysis for Carbon in Sodium, Feb. 23, 1962.

d. Oxygen Analysis of Sodium

The conventional methods for the analysis of sodium for oxygen involve the separation of the bulk of the sodium from the oxygen-containing compounds either by dissolution in some solvent (for example, mercury or ammonia) or by vacuum distillation. The residue is analyzed for oxygen or sodium (assuming the residue is Na_2O). These methods suffer the usual disadvantages inherent in methods that require a small amount of a substance to be separated quantitatively from a large excess of a very reactive constituent. Extreme care is required to reduce the extent of contamination. These methods appear to give qualitative results in the 10-15 ppm range and quantitative results above 50 ppm.

Activation methods offer the possibility of reducing the limit of detection and improving the accuracy. Work has continued on the method for the analysis of oxygen in sodium which utilized the $^{16}\text{O}(\text{n,p})^{16}\text{N}$ reaction. The 7.3-second ^{16}N activity has a prominent 6.1-Mev gamma ray which, along with its escape peaks, is readily measured using a gamma ray spectrometer.

In practice, the sample is irradiated in a fast-neutron flux ($\sim 1.5 \times 10^8 \text{ n/cm}^2\text{-sec}$) for about 0.5 min, transferred (0.04-min transit time) via a pneumatic system, and counted for 0.5 min. By using two 4-in. x 4-in. NaI (Tl activated) detectors, a sensitivity of about 400 counts per milligram of oxygen was obtained. Irradiation of a number of elements showed the only possible interferences to be fluorine and boron which are not likely to be present in sodium.

The sensitivity of the method may be improved by increasing the effective flux by the use of a different generator and increasing the counting efficiency by counting the 10.5-Mev beta associated with 28% of the decays. The intrinsic counting efficiency for beta counting is nearly 100%, compared to about 5% for gamma counting.

The method is limited mostly by the lack of a sample container of suitably low oxygen content. A number of low-oxygen polyethylenes have been tested, and all were found to contain 200 to 300 ppm of oxygen. A mechanical solution to this problem is being investigated. A sample container has been designed which will permit the sample to be irradiated at one end and counted at the other end.

D. Fuel Processing Facility for EBR-II

Construction of a fuel reprocessing-refabrication plant (Fuel Cycle Facility) for the recovery of fuel from the EBR-II reactor was completed during 1962. During 1963, the service equipment, installation of which had been completed in 1962, was placed in operation, and most of the processing

Figure I-25

EBR-II FUEL SUBASSEMBLY (shown with component parts)

EBR II FUEL ELEMENT

EBR II FUEL SUBASSEMBLY

equipment was installed. The development of equipment for the Fuel Cycle Facility has been a joint effort of the personnel of the Central Shops Department, Remote Control Engineering Division, Metallurgy Division, Reactor Engineering Division and Chemical Engineering Division. However, for the sake of completeness, all of the major equipment items now installed in the Fuel Cycle Facility are described below.

The Fuel Cycle Facility, which is located adjacent to the EBR-II reactor, will make possible the operation of the EBR-II reactor on a closed fuel cycle, that is, the spent fuel subassembly (Figure I-25) will be removed from the EBR-II reactor and transported to the Fuel Cycle Facility where it will be disassembled, processed, refabricated, assembled and returned to the EBR-II reactor. All process steps will be carried out by remote means. Pyrometallurgical methods will be used to recover the fertile and fissionable materials from the partially spent fuel. The facility will also be used as a pilot plant for the evaluation of new or improved pyrometallurgical recovery processes and fuel refabrication methods. Figure I-26 is an isometric sectional view of the Fuel Cycle Facility.

Figure I-26

ISOMETRIC SECTIONAL VIEW OF THE FUEL CYCLE FACILITY

In the Fuel Cycle Facility, the equipment for processing, fabrication, and assembly of reactor fuel elements and subassemblies will be contained in two heavily shielded, interconnected cells, one with an air atmosphere (Air Cell) and the other with an argon atmosphere (Argon Cell). The Air Cell will be used for operations which do not involve exposed, potentially pyrophoric materials (sodium, fuel). Typical operations in the Air Cell include the disassembly of spent fuel subassemblies and the assembly of new subassemblies. Figure I-27 is a photograph of the inside of the Air Cell, showing some of the installed processing equipment.

Figure I-27

AIR CELL AND PROCESS EQUIPMENT

The Air Cell will be used to disassemble partially spent EBR-II fuel subassemblies, to test refabricated fuel elements and to assemble them into subassemblies for return to the EBR-II reactor. The spent EBR-II fuel subassembly will be transported in an interbuilding fuel coffin from the EBR-II reactor. The subassembly will then be removed from the interbuilding coffin and brought into the Air Cell through an opening in the cell floor (not visible here) and will be placed in the dismantler seen along the left wall where the subassembly will be disassembled. Sodium bonding equipment and testing equipment for refabricated fuel elements are shown along the right wall. Temporary storage of spent and refabricated subassemblies will be provided by ten-foot deep storage pits covered by the discs seen in the center foreground. The small transfer locks are in the background (mounted horizontally in the shielding wall between the Air Cell and the Argon Cell). A machine for assembling refabricated fuel elements into subassemblies is to be installed.

Figure I-28

ARGON CELL TRANSFER LOCKS AND FUEL ELEMENT DECANNING (AND PIN CHOPPING) EQUIPMENT

Transfer of materials between the Air Cell and the Argon Cell will be made through either a large transfer lock (right background) or two small transfer locks (center background). After an EBR-II fuel subassembly has been disassembled in the subassembly dismantler in the Air Cell, the fuel elements will be transferred to the Argon Cell through the small locks. The fuel elements will be placed in the spiral decanner and pin chopper (foreground) where the stainless steel jackets will be removed and the uranium fuel pins cut to proper length for use in the melt refining furnace.

Process equipment for the Argon Cell, which will be used for all operations that involve the handling of exposed, potentially pyrophoric materials, such as the decanning of fuel pins, purification of irradiated fuel, fabrication of new fuel pins, and assembly of fuel elements, has been installed. Photographs of the decanning equipment and fuel purification equipment are shown in Figures I-28 and I-29, respectively. This equipment was installed during 1963. Refabrication equipment is illustrated in Figures I-30 and I-31.

Processing operations in the Air Cell and the Argon Cell will be observed and controlled from operating areas outside the process cells. The operating areas (see Figure I-26) are along the walls of the Air Cell and along the outer wall and the inner wall (Central Control Room) of the Argon Cell.

Figure I-29

ARGON CELL MELT REFINING AND PIN CASTING EQUIPMENT

The chopped fuel pins will be moved from the spiral decanner (and pin chopper) and charged into a melt refining furnace (under metal bell jar seen in the center foreground) where the pins will be melt refined, after which the purified molten uranium will be poured into a graphite mold. The refined ingot will be removed from the mold by means of an ingot remover and sampler (left foreground). The ingot will then be transferred to an injection casting furnace (tall metal bell jar seen in center background) for melting and casting into fuel pins (see Figure I-25), which will be carried out by pressurizing the furnace to force the molten uranium into Vycor glass mold tubes. A bank of service feed throughs is seen at floor level between the melt refining furnace and the ingot remover and sampler. Steel shutters to protect the windows from radiation damage when the windows are not in use are seen hanging from the window shutter rails above the shielding windows.

Service equipment which might become radioactively contaminated is installed in the subcell area on the service floor. This area, extending under most of the Argon Cell, is separated from the service floor by a two-foot thick concrete wall.

1. Argon Cell Atmosphere

Because highly reactive nuclear fuel and scrap fuel materials will be handled in the Argon Cell, the specifications for the atmosphere in the Argon Cell were established at less than 100 parts per million of oxygen

Figure I-30

ARGON CELL FUEL PIN PROCESSING EQUIPMENT

The pins will be moved from the injection casting furnace (tall metal bell jar in the center foreground) to pin processing machines (foreground) where the following operations will be carried out: the Vycor glass mold material will be removed from the pins, the fuel pins will be cut to length and inspected for diameter, length, weight and porosity. The melt refining furnace is seen in the background.

and less than 5 parts per million of water vapor. The potentially high concentration of volatile fission products in the Argon Cell atmosphere makes it desirable to operate the cell at a pressure lower than the pressure in the surrounding areas. Because of these two factors, the Argon Cell was constructed to insure a low rate of air in-leakage and was provided with a purification system for removing oxygen and water vapor from the argon atmosphere. The equipment items for the argon purification system include a compressor, a catalyst (palladium) bed, and a desiccant bed. In the catalyst bed, the oxygen is catalytically reacted with added hydrogen to form water vapor. The water vapor formed by the catalytic reaction and the water vapor present in the argon atmosphere are removed by the desiccant bed.

On January 16, 1963, the Argon Cell was sealed and a nitrogen atmosphere was established. The purpose of this operation was to determine accurately the air in-leakage rate to the cell by measuring the rate of rise in oxygen concentration in the cell atmosphere, and to test the operation of

Figure I-31

ARGON CELL FUEL ELEMENT ASSEMBLY STATION AND FUEL ELEMENT WELDING EQUIPMENT

The fuel pins will be moved from the pin processing machine to the fuel element assembly table seen in the right background where they will be placed in the stainless steel cans which will contain the proper weight of bonding sodium. The assembled elements in a magazine (20-pin capacity) will be transferred to a settler (seen at notched corner of assembly table) where the fuel elements will be heated to distribute the sodium inside the assembled elements. After the sodium has been melted, the restrainer plugs (see Figure I-25) will be added. The assembled elements in a magazine will then be transferred to the welding machine where a gas-tight closure of the stainless steel can will be made. The magazine will be placed over the pedestal in the welding machine, and one element at a time will be welded. The welding machine, with a loaded magazine in front of it, is in the center foreground.

the temperature-pressure control equipment, the argon purification system equipment, and process auxiliary equipment, such as lights, manipulators, viewing devices and transfer facilities. After repair of many small leaks, the in-leakage rate met the design goal of less than 0.01 cfm at a cell pressure of two inches of water below atmospheric pressure. An air atmosphere was reintroduced in the Argon Cell on March 9, 1963.

On August 8, 1963, operations were begun to establish an argon atmosphere in the Argon Cell. About 80,000 standard cubic feet of argon were available for purging and filling the 65,000 cubic foot cell (the gas content of the cell at 80°F and 12.2 psia is equivalent to 53,000 scf). The purging

operation reduced the air concentration to five percent. The Argon Cell purification system was then placed in operation to reduce further the oxygen concentration of the argon gas. The flow rate through the purification system was 175 scfm. After nine days of operation of the purification system, the concentrations of impurities in the cell argon were as follows: nitrogen, about 4.3%; oxygen, less than 50 ppm; and water, less than 200 ppm.

The purification system is usually operated only during the day shift; therefore, the oxygen concentration in the cell argon rises during the night and during the week-end as a result of air in-leakage. Periodically, the rate of air in-leakage was determined by noting the rate of increase in the oxygen concentration during an overnight period. During these air in-leakage test periods, the addition of hydrogen to the catalyst bed was stopped so that there was no oxygen removal, and the pressure in the cell was maintained at a negative pressure of 2 to 4 inches of water. By mid-September the test results showed that the rate of air in-leakage had been reduced to 0.0048 scfm.

The intermittent operation of the purification system results in an oxygen concentration of about 50 ppm. However, calculations showed that if the purification system was operated continuously (with addition of the stoichiometric requirements of hydrogen) and the in-leakage rate was 0.0048 scfm, the concentration of the oxygen in the cell could be reduced to 6 ppm and maintained at this level. The advantages of maintaining the oxygen concentration at this low level would not, however, compensate for the additional work required for continuous operation of the purification system.

Personnel entered the Argon Cell while the cell contained an argon atmosphere in order to effect repairs on the cell manipulators. Thirteen separate entries were made by individuals wearing self-contained air masks (Scott Air Pak*) and carrying air bottles, each having a capacity of 40 cu ft. Each entry and exit required four minutes, and the useful working time per entry averaged 14 minutes. The thirteen entries introduced a total of 2200 cubic feet of air into the cell. This resulted in a maximum water vapor concentration of 250 ppm, and maximum nitrogen and oxygen concentrations (estimated) of 7.9 and 0.8%, respectively. Four days after the last entry, the argon atmosphere contained 7.2% nitrogen, and only 10 ppm oxygen and 40 ppm water vapor. During the entire operation, the cell pressure was maintained at or slightly above atmospheric pressure.

2. Process Equipment Installation and Start-Up

The Air Cell will be used for the disassembly of spent fuel sub-assemblies, the testing of refabricated fuel elements (such as leak-testing

*A product of Scott Aviation Corporation.

and sodium bond- and sodium level-testing), and the reassembly of new assemblies. After disassembly of the fuel subassembly, the fuel elements (Figure I-25) will be transferred to the Argon Cell. A spiral decanner and pin chopper* (Figure I-28) will remove the stainless steel can and cut the fuel pins into required lengths for charging to the melt refining furnace (Figure I-29), where radioactive impurities will be removed from the fuel. The refined metal fuel will then be recast into fuel pins in the injection casting equipment** shown in Figure I-30.

Operational tests are currently being carried out on the spiral decanner and pin chopper. These tests are also giving personnel experience in the use of the equipment. Unirradiated fuel elements containing depleted uranium-fissium alloy pins which are sodium-bonded to the stainless steel fuel element cans are being employed in the tests. The cut pins from the machine are used as charges to the melt refining furnace.

The adherence of sodium to various moving parts of the machine has caused some difficulty in its operation. Tests have been carried out in which water was added to the argon atmosphere of the Argon Cell to determine if increased water concentrations above the initial 5 ppm would improve the operation of the machine. Preliminary results indicate that the operation of the machine is improved if the concentration of water in the cell atmosphere is increased above 20 ppm. Seven runs have been made in which pins were prepared for use as melt refining charges.

The processing of 19 charges, each of which consisted of approximately 8 kg of unirradiated, uranium-fissium chopped fuel pins, has been carried out by remote means in a melt refining furnace in the Argon Cell. The primary purpose of the runs was to consolidate chopped pins into ingots suitable for use in the injection casting furnace. The poured yields varied from 85.6 to 96.9 w/o, most of the yields being about 95 w/o. Sodium adhering to the fuel pins was collected in a fume trap which covers the crucible. Operation of the furnace was considered satisfactory.

A number of runs were made in the injection casting furnace using uranium-fissium alloy material. The injection casting furnace converts the melt-refined ingots into sound cylindrical castings for producing fuel pins for fuel elements. By means of injection or pressure casting of molten fuel into precision-bore Vycor (silica) tubes or molds, fuel pin castings of finished diameter but of excess length are produced. In this casting operation, the fuel is melted in a closed evacuated furnace, and the molten fuel is then forced, by pressurizing the furnace, up into vertically suspended molds where the molten fuel solidifies to form the castings. Operation of the equipment was considered to be satisfactory.

*Developed by Remote Control Engineering Division, Argonne National Laboratory.

**Developed by Metallurgy Division, Argonne National Laboratory.

The subassembly dismantler* (Figure I-27) has been installed by remote means in the Air Cell. This machine is designed to disassemble remotely all seven types of subassemblies currently planned for use in the EBR-II reactor. One disassembly run was made with a subassembly similar to that shown in Figure I-25. Although the need for adjustment and for minor changes was indicated, the machine appears to be capable of performing its function.

An 18-ton interbuilding fuel transfer coffin has been designed and built by Argonne National Laboratory for transporting fuel subassemblies between the Reactor Building and the Fuel Cycle Facility. The coffin provides up to 13 inches of lead shielding, and is capable of removing the 1 kw of fission product heat which is generated within a subassembly that has been irradiated to 2% burnup in 135 days and cooled for 15 days. Cooling of the subassembly is accomplished by circulating a stream of argon or air down through the subassembly and then up through an annular heat exchanger to transfer the heat to the shielding lead. The gas is circulated by means of a lobe-type blower which is driven by a battery-powered, 1-1/4 hp, 32-volt d-c motor and can deliver about 30 cfm of gas. Two views of the coffin are shown in Figures I-32 and I-33.

Figure I-32

FUEL TRANSFER COFFIN. FRONT VIEW

Figure I-33

FUEL TRANSFER COFFIN. REAR VIEW

*Developed by Remote Control Division, Argonne National Laboratory.

Design criteria for the coffin limit the maximum temperature of the center fuel pin in a subassembly to 600°F. To demonstrate the cooling performance of the coffin, a mock subassembly containing resistance heaters in place of fuel pins was employed under varying conditions of heat input and gas flow. The results of the tests (shown in Figure I-34) demonstrate that the cooling system of the coffin is more than adequate to remove the fission product decay heat from a spent fuel subassembly.

Figure I-34

HEAT REMOVAL PERFORMANCE TESTS ON INTERBUILDING FUEL TRANSFER COFFIN

(Resistance-heated core subassembly used to simulate irradiated subassembly. Coolant: air or argon.)

During transfer to the Fuel Cycle Facility, the subassembly must be cleansed of the film of sodium which covers it (see ANL-6766, p.65). The stepwise procedure involves converting the sodium to oxide, then to hydroxide and finally removing the hydroxide with water and drying the subassembly and coffin with air. This operation has been performed successfully on a number of unirradiated fuel subassemblies.

Two racks have been installed in the Air Cell floor pits (Figure I-27) for the temporary storage of up to eight subassemblies (spent or re-fabricated). Coolant air for the two racks is provided by two blowers located outside the cell. Each blower can deliver 135 cfm of air, which is sufficient for cooling eight subassemblies. The blowers will be operated with one unit in stand-by condition. Automatic controls will place the stand-by blower in service should the operating blower fail.

3. Materials Testing

At the conclusion of the period during which the Argon Cell was filled with nitrogen, the drive motors (direct current; 1/4 hp) for the manipulator grips were examined. An extremely high rate of brush wear was discovered. Although the total running time of these motors in the dry nitrogen atmosphere (as low as 5 ppm water and 8 ppm oxygen) was an hour or less, brushes were worn more than 0.218 inch, which is the maximum allowable wear. The results of earlier brush tests made in an argon atmosphere indicated that the wear rate of similar brushes was satisfactory. These earlier tests, however, were conducted in a small volume test chamber in which it was difficult to maintain an atmosphere of low moisture content for long periods of time. Apparently, the slow drying of the brushes in the Argon Cell during the extended period of exposure to a low moisture-content atmosphere created the condition for rapid brush wear.

Brush tests are now being conducted in a large volume glove box containing an argon atmosphere which is continuously monitored for oxygen and moisture. Brushes are being tested in a pair of motors which are coupled together so that one motor drives the second one, which acts as a generator. The load on the generator is adjusted to impose a controlled load on the driving motor. The motors are identical to those currently being used in the Argon Cell manipulators and those used in the previous tests.

Tests on several types of brushes have been conducted. A resin-bonded carbon-graphite brush containing 5% molybdenum disulfide (Stackpole grade 660*) showed the least wear. In an argon atmosphere containing 2 to 21 ppm moisture and less than 20 ppm oxygen, the highest wear rate for this grade brush was 0.018 in./hr.

In additional tests with the Stackpole grade 660 brushes, an attempt is being made to correlate brush wear with motor operating characteristics and to determine the effect on brush wear rate of different concentrations of oxygen and moisture in the range 0 to 100 ppm.

*A product of Stackpole Carbon Company, St. Mary's, Pennsylvania.

4. Equipment Development for EBR-II Skull Reclamation Process

After irradiated EBR-II fuel has been purified by melt refining and has been poured from the melt refining crucible, a mixture of uranium and fission product oxides and some uranium metal remain in the crucible. The uranium in this residue or skull will be recovered and purified by the skull reclamation process. This recovery and purification is important to the economics of the fuel cycle and also provides uranium of sufficiently high purity to allow its use as a make-up stream to the melt-refined fuel for the purpose of adjusting the concentrations of noble fission product elements which are not removed by the melt refining process. The composition of the fuel can thus be maintained constant from one fuel processing cycle to the next.

The skull reclamation process is also expected to be applicable to the recovery of fissionable materials from casting heels, pin croppings, and other materials which might be unsuitable for direct introduction to the melt refining process. The process may also, with suitable modification, permit direct processing of metallic uranium, oxide, nitride and carbide fuels. The process consists of conversion of the uranium to oxide, removal of noble metals from the uranium oxide, reduction of the uranium oxide, and recovery of the uranium.

a. Furnaces for EBR-II Skull Reclamation Process

The material (skull) remaining in the crucible after melt refining adheres to the crucible walls and cannot be easily removed. It has been found, however, that on oxidation, the skull is transformed to a powder which is readily poured from the crucible. The plant-scale equipment for converting the skull into a pourable oxide powder has been designed, built, operationally tested and installed in the Argon Cell. The equipment consists of an oxidation furnace, a control system for the oxidizing process, and a mechanism (dumper) for transferring the oxide powder from the melt refining crucible to a storage container.

Zinc cans have been developed for containing and storing the skull oxide powder prior to charging it into the skull oxide-processing furnace. The use of these cans eliminates the need for a powder charging mechanism since the can and its oxide powder can be placed in the furnace by means of the Argon Cell manipulators. The zinc can then becomes a part of the process materials.

A design for a plant-scale (5 kg of skull oxide) induction-heated furnace for skull oxide processing has been proposed in which the shell (atmosphere enclosure) of the furnace acts as the susceptor. The shell is surrounded by a layer of insulation which is removable. The induction coil is located around the insulation. This arrangement provides

good cooling for the induction coil and protects the coil against the deleterious effects of process fumes. It also allows rapid cooling of the crucible through the mechanical removal of the insulation. Tests are underway to determine the feasibility of this concept and to provide a basis for selection of materials for furnace construction.

b. Magnesium-Zinc Distillation Studies

Uranium coated with magnesium-zinc is the product from the uranium precipitation step of the skull reclamation process. The uranium will be recovered from this material by distilling off the volatile magnesium-zinc. Distillation equipment for carrying out an investigation of this process step has been developed and tested on a scale of 3 kg of distillate. A plant-scale distillation apparatus (see Figure I-35), suitable for handling 36 kg of distillate, has also been built, but has not yet been tested. (A maximum of 36 kg of Zn-12 w/o Mg will be associated with 5 kg of uranium, which is the anticipated batch size.) The main components of the distillation apparatus (3-kg and 36-kg scale) are a graphite condenser, graphite distillate collector, process crucible, graphite secondary (crucible enclosure), and graphite secondary cover. Except for the distillate collector, and possibly the condenser, all of these compounds are re-usable. The purpose of the graphite felt insulation inside the distillate collector and the insulation between the distillate collector and the secondary cover is to prevent reboiling of the collected distillate.

Figure I-35

MAGNESIUM-ZINC DISTILLATION APPARATUS 36-KILOGRAM SCALE

There are two features (see Figure I-35) other than size, which make the design of this distillation apparatus significantly different from the distillation equipment described previously (see ANL-6766, p. 69). First, the seal between the distillate collector and the secondary cover has been changed to a butt joint. This type of joint was tested in the smaller scale equipment in eight runs in which magnesium-zinc distillate were collected. The butt joint prevented leakage and was easily separated after each experiment. In the new apparatus, a graphite secondary cylinder has been added to contain the process crucible, and the cover fits onto the secondary. This feature retains the high-quality seal that is possible when readily machineable graphite parts are mated, and now permits the use of a crucible fabricated from materials other than graphite. The graphite secondary is shorter than the crucible to permit pouring molten uranium product from the crucible.

Distillation and collection of magnesium-zinc has been successfully demonstrated on the 3-kg scale. No serious scale-up problems are anticipated in the distillation and collection of the magnesium-zinc vapors. However, consolidation and recovery of the uranium product still remain to be demonstrated. Distillation equipment is being installed in an inert atmosphere (argon) glove box to carry out an investigation of this step of the skull reclamation process.

E. Preparation of Fuels for Fast Reactors

1. Solid Fuels

Refractory compounds of the actinide elements, such as carbides and sulfides, show promise as reactor fuels capable of withstanding high temperatures and large burnups. Methods are being investigated for the preparation of these refractory fuels, and the more promising methods are being used to prepare sufficient quantities of these fuels for fabricability evaluations and irradiation testing by the Metallurgy Division.

a. Preparation of Uranium Carbide

The method and facilities for the preparation of uranium monocarbide have been described previously (ANL-6766, p. 41). Carbon is added to a zinc-magnesium solution of uranium at 750-800 C, uranium monocarbide is precipitated, and magnesium and zinc are removed from the carbide by siphoning and distillation steps. Because of the excellent pressing and sintering properties of the uranium carbide powder prepared by this method, considerable interest has developed in this process, and it was scaled up to produce 0.5-1 kg of uranium monocarbide per batch for fuel element fabrication and irradiation tests by the Metallurgy Division.

Since the last report period, work has been concentrated primarily on the refinement of the process to give a lower oxygen content and improved stoichiometry of the uranium monocarbide. The oxygen content has been successfully reduced below the limit (0.2 w/o oxygen) specified for the UC fuel by the Metallurgy Division; however, the carbon content is slightly above specifications (5.2 w/o carbon). Process variables are being studied which may lower the carbon content in future preparations of uranium monocarbide. The best material prepared to date analyzed 0.14 w/o oxygen (now limited by the oxygen content of the carbon used in the process) and 5.6 w/o carbon (theoretical for UC = 4.8 w/o carbon). Approximately 800 g of enriched UC (93% U^{235}) will be prepared in the near future for the Metallurgy Division's fuel irradiation program.

In addition to the above work, apparatus is being assembled to study the conversion of powdered uranium metal to uranium monocarbide in a fluidized bed, using a mixture of methane and hydrogen as the reactant and fluidizing gas. The ratio of methane to hydrogen used initially will be such that free carbon would not form at thermodynamic equilibrium. A fluidized bed of uranium carbide and hydrogen will also be evaluated as a means of removing excess carbon in uranium monocarbide preparations. At elevated temperatures ($>600^{\circ}\text{C}$), hydrogen will react with the excess carbon to form volatile hydrocarbons and hydrocarbon radicals.

b. Preparation of Plutonium-Uranium Carbides

Plutonium monocarbide cannot be prepared by the liquid metal method for preparing uranium monocarbide, described in the previous section, because plutonium carbides are not stable in the presence of significant quantities of zinc at the process temperatures. An attempt to prepare plutonium monocarbide by adding carbon to a molten plutonium-magnesium alloy resulted instead in the production of plutonium sesquicarbide (Pu_2C_3). The material prepared by the conventional high temperature carbon reduction of the oxide (for example, arc melting) produces a product that is difficult to fabricate. For these reasons, new preparative methods are being investigated.

One of the methods currently being studied is the reaction of UCl_3 and PuCl_3 with Mg_2C_3 in a molten salt mixture (LiCl-MgCl_2). In preliminary experiments with PuCl_3 , however, Pu_2C_3 was formed rather than the desired monocarbide. Further work with plutonium is required in order to evaluate adequately the method as a means of preparing PuC and solid solutions of UC and PuC.

c. Preparation of Uranium Monosulfide

The preparation method of Eastman and coworkers¹² was used to produce US in batches of 100 to 300 g for the Metallurgy Division's reactor fuel evaluation program. This method consists of three steps: (1) bulk uranium metal is hydrided and dehydrided to produce finely divided uranium metal powder, (2) the uranium powder is treated at 400 to 500°C with the stoichiometric quantity of H₂S required to form US, and (3) the resulting mass of metallic uranium and higher uranium sulfides is ground, sieved, mixed, and heated in vacuum at 1900°C for about two hours to form homogeneous US. All steps of the preparation are conducted in vacuum or under high-purity inert atmospheres to avoid contamination of the product.

Previous preparations of US on a smaller scale had produced a product of inadequate purity, as indicated by chemical analyses and lattice parameters obtained by X-ray diffraction. The impurities, mainly nitrogen and carbon, proved to be contaminants of the H₂S that was used. By condensing the H₂S in a liquid nitrogen cold trap under vacuum, the levels of these impurities were reduced substantially.

Analytical data for the current preparations of US are listed in Table I-11. Variations in the sulfur-to-uranium ratio from 0.95:1 to 1.04:1 should provide a reasonable range for determination of the effect of this parameter on the sintering characteristics of the material. Lattice parameters of 5.489 or 5.490 Å were obtained for products in which the sulfur-to-uranium ratios were between 0.99:1 and 1.02:1. At both higher and lower sulfur-to-uranium ratios, the lattice parameter decreased. These data indicate that uranium sulfide is a solid solution at room temperature over the composition range of $0.99 < S/U < 1.02$. This result confirms the data of other investigators,¹³ who reported a range of solubilities in this region of the uranium-sulfur system, and obtained a lattice parameter of 5.490 Å.

Since UC and UN have the same structure as US, but much smaller lattice parameters, the presence of these impurities as solid solutions should result in a decreased lattice parameter of the US product. The effect of oxygen contamination is more obscure. However, the results from Runs 51, 57 and 58, which all show sulfur-to-uranium ratios of 1.02:1, indicate that the limited variations in impurity content for these three runs did not affect the lattice parameters appreciably. The data in Table I-11

¹²E. D. Eastman, Brewer, L., Bromley, L. A., Gilles, P. W. and Lofgren, N. L., J. Am. Chem. Soc., 72, 4019 (1950).

¹³A value of 5.490 Å is reported by Cater for uranium monosulfide: E. D. Cater, P. W. Gilles, and R. J. Thorn, J. Chem. Phys., 35, 608 (1961).

Table I-11

ANALYSES OF URANIUM MONOSULFIDE PREPARATIONS

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

Run No.	Total ^a Uranium (w/o)	Total ^b Sulfur (w/o)	S/U ^c	Lattice Parameter (Å)	Insolubles (w/o)	O ₂ (w/o)	N ₂ (w/o)	C (w/o)
52	87.50	12.20	1.04	5.485	<0.01	0.088	<0.0010	0.038
66	87.57	12.18	1.033	5.485	0.04	0.022	0.002	0.020
60	87.68	12.20	1.03	5.487	0.03	0.045	<0.0010	0.043
51	87.96	12.06	1.02	5.490	0.03	~0.2	0.0053	0.017
57	87.90	12.10	1.02	5.490	0.19	0.09	<0.0010	0.013
58	87.89	12.03	1.016	5.490	0.13	0.12	0.011	0.042
64	87.81	11.92	1.008	5.487	0.12	0.024	0.0015	0.019
65	87.95	11.92	1.006	5.488	0.22	0.068	0.0010	0.039
59	87.95	11.88	1.003	5.489	0.09	0.075	0.0024	0.063
62	88.02	11.86	1.00	5.489	0.01	0.095	0.0017	0.057
54	87.98	11.73	0.99	5.489	0.03	0.21	0.007	0.028
61	88.22	11.64	0.99	5.489	0.73	0.14	0.0018	0.045
55	88.10	11.62	0.98	5.485	0.19	0.13	0.009	-
56	88.42	11.29	0.95	5.484	1.3	0.13	0.006	-

^aDetermined by oxidation of the sulfide to U_3O_8 .

^bDetermined gravimetrically, after oxidation of sulfide to sulfate.

^cCorrected for insolubles.

suggest that the sulfur-to-uranium ratio has a greater effect on the lattice parameter of the US product than do the small amounts of impurities which were present. Spectrographic data indicated that there was no significant pickup of metallic impurities during the preparation of the US.

Approximately 2 kg of US has been prepared and made available to the Metallurgy Division for their fuel irradiation and fabrication tests. Preparative work on US in the Chemical Engineering Division has been discontinued.

2. Mobile Fuels and Blankets

Mobile fuels and blankets, such as slurries, pastes, molten salts, and molten alloys, are currently being evaluated as to their potential in fast breeder reactors. If any of these systems show sufficient promise, a modest research and development program will be established.

The potential advantages of mobile systems relate primarily to reduced fuel and blanket fabrication and handling costs, and to reduced reactor down-time. Solid fuels contribute significantly to reactor down-time because of the need to periodically move blanket and fuel rods in order to attain more uniform breeding and fuel burnup. Because of their high coefficients of thermal expansion, mobile fuels may also contribute to the safety of fast reactors. This work has not progressed to the point where program recommendations can be made.

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

Interest in the fluoride volatility processes as a promising alternative to the existing aqueous solvent extraction processes continues to be high, both in the U.S. and in Europe. In December 1963, the AEC announced that, in response to interest expressed by industry, it was making available technical data and other information relating to fluoride volatility methods for reprocessing nuclear fuels. The AEC also indicated that, as a part of the development program, it is possible that some type of demonstration plant program may be undertaken at a future date. A technical information meeting for interested industrial firms was scheduled for Spring 1964 at Argonne.

In the fluoride volatility processes, uranium and plutonium in spent nuclear fuels are converted into hexafluoride compounds which are volatile and can therefore be separated from fission products and from cladding and alloying materials by techniques such as vaporization and distillation. These processing methods offer a number of advantages over the solvent extraction processes, one of the most important being that the radioactive waste products are in solid form and small volume. Other advantages include (1) the ease of separation of UF_6 from impurities, (2) the absence of reagents susceptible to deleterious radiation effects, (3) virtual absence of neutron moderating chemicals, and (4) reduction in the costs of converting uranium and plutonium to final usable forms. While the economics of volatility versus aqueous technology is not yet clearly defined, studies in this direction are underway.

Until recently, the volatility process development program at Argonne was directed primarily toward recovery of reactor fuels having a high content of uranium-235. Subject to continued success in the development program, it is felt that volatility technology may in due course be capable of processing civilian power reactor fuels and thus become an essential part of a competitive private chemical processing industry.

A. Engineering-Scale Investigations

1. Processing of Nuclear Reactor Fuels of High Enrichment

Many nuclear reactors, such as research or test reactors, mobile power reactors and others, employ fully enriched uranium as the fuel. The most important types of the high enrichment fuels at the present time consist of uranium alloyed and clad with either aluminum or Zircaloy-2.* The spent fuels contain uranium in concentrations below 10% and plutonium concentrations which are too low to warrant recovery. The separation problem, therefore, is one of separating uranium from bulk constituents of the fuel and from

* Zircaloy-2 is a high-zirconium alloy containing about 1.5% tin, 0.15% iron, 0.10% chromium, and 0.05% nickel.

fission products and plutonium. A high-recovery, high-decontamination process is under development, in which chemical separation of the fuel constituents and subsequent recovery of the uranium is achieved by selective volatilization of chlorides and fluorides.

The conceptual process involves hydrochlorination of the alloy while it is submerged in a fluidized bed of inert solids (high-fired alumina), and then, fluorination of the system to separate uranium as the hexafluoride, both reactions being conducted in the same vessel. The hydrochlorination step effects a separation of the uranium from the alloying material and also from the cladding, since these are of the same material. The separations occur through the formation of the volatile chlorides of zirconium and aluminum (sublimation points at 1 atm for ZrCl_4 and AlCl_3 are 331°C and 180°C , respectively), while the uranium remains in the system as nonvolatile chlorides. Entrained uranium and other particulate solids are retained in the system by a packed bed of alumina which serves as a high-temperature filter. The uranium is subsequently recovered as the hexafluoride (sublimation point at 1 atm for UF_6 is 56.6°C) during the fluorination step. The progress of the reactions is followed continuously by measuring the concentration of key components in the off-gas stream by the use of in-line thermal conductivity cells. Since both the hydrochlorination and fluorination reactions are highly exothermic, the use of a fluidized bed, because of its excellent heat transfer characteristics, permits nearly isothermal conditions to be maintained at high reaction rates. Final decontamination of the uranium hexafluoride would be accomplished by adsorption-desorption on beds of sodium fluoride, a process which has been successfully demonstrated by other workers.¹ The volatile chlorides of zirconium and aluminum are hydrolyzed in a fluid-bed pyrohydrolysis reactor to the oxides for ease of disposal.

Work with unirradiated fuel material is being carried out at both a bench-scale level (1 1/2-in. dia. reactor) and a pilot-scale level (6-in. dia. reactors). The latter facility is capable of demonstrating the processing of up to 30-kg charges of uranium-Zircaloy or uranium-aluminum alloy in the form of multiplate assemblies.² A schematic diagram of the pilot plant facility is shown in Figure II-1. A bench-scale facility for work with highly irradiated material is being installed in the Senior Cave in the Chemical Engineering Building and is expected to be in operation by summer of 1964.

¹Milford, R. P., Process Developments in the ORNL Fluoride Volatility Program, Oct. 1962 to Sept. 1963, ORNL-TM-717.

²For a description of the fuel, see Westinghouse Electric Corp., The Shippingport Pressurized Water Reactor, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1958).

Figure II-1

HIGH ENRICHMENT URANIUM ALLOY VOLATILITY PROCESSING PILOT PLANT

Previous bench-scale studies (see ANL-6766, p. 77) had established the processing conditions necessary for satisfactory operation and for high uranium recovery from uranium-Zircaloy fuel materials. More recent work has extended these studies to uranium-aluminum alloy materials. The operating conditions which have been established for the latter material are virtually identical to those for zirconium alloys, except that the operating bed temperatures during hydrochlorination are approximately 300 °C instead of 400 °C. At this bed temperature, the metal fuel plate temperature remains well below the melting point of aluminum (660 °C) during hydrochlorination.

Correlation of the experimental data from bench-scale studies with zirconium alloys indicated that the uranium loss through the packed-bed filter

during hydrochlorination is a function mainly of the lowest temperature downstream of the fluid bed (but within the system comprising the reactor and the packed-bed filter). A semi-log dependency was found (see Figure II-2), indicating that loss by vaporization is the probable mechanism. The probable

Figure II-2

URANIUM LOSS DURING HYDROCHLORINATION OF URANIUM-ZIRCONIUM ALLOY FUELS

Average rate of uranium loss vs $1/T$, where T ($^{\circ}\text{K}$) is measured in the reactor assembly and is the lowest temperature encountered by the gases after leaving the fluid bed.

vaporizing species is uranium tetrachloride (since the vapor pressure of uranium trichloride is negligible in this temperature range of 320 to 390 $^{\circ}\text{C}$). Calculations based on reported values for the vapor pressure³ of uranium tetrachloride indicate that the exit gas was about 50 percent saturated under most of the run conditions. The main conclusion to be drawn from this information is that, to minimize losses, the unit should be operated at as low a temperature as possible, especially in the region of the disengaging section above the fluid bed, in the connecting line between the process reactor and the packed-bed filter, and in the filter itself (see Figure II-1). These results further suggest that the solution of the overall problem of retaining uranium in the system may not depend on filtration alone, but rather on a combination of filtration and condensation of a volatile species, with the latter being possibly of greater importance. For both aluminum and zirconium alloy fuels, the uranium losses during hydrochlorination have been maintained at a level of about 0.2% or less by maintaining the filter-bed temperature at 335 $^{\circ}\text{C}$ or lower, at which temperature the volatility of UCl_4 is very slight.

Losses due to retention of uranium by the alumina beds in the reactor and filter after fluorination of both types of fuel were also at a low level (about 0.5%),

³Stoller, S. M., and R. B. Richards, Reactor Handbook, Vol. II, Fuel Reprocessing, Interscience Publishers, Inc., New York (1961), p. 267.

the final concentrations of uranium in alumina being about 0.01 w/o or less. This level of uranium loss was maintained when the same alumina beds were used for hydrochlorination of three batches of fuel material, after which the uranium was recovered in a single fluorination.

A study in which fission product elements* were added along with the fuel alloy during processing indicated that there was no tendency for the alumina in the fluid-bed reactor to cake even under severe conditions of temperature cycling imposed when the bed was in a static condition. This result lends support to the reliability of operation of this process. Behavior of the fission product elements followed the expected pattern, that is, their disposition during each step was found to correspond to that expected from the known volatility of their higher valent chlorides or fluorides. Tests with a prepared alloy containing added fission elements will also be made prior to experiments with irradiated material.

Studies directed toward process simplification and improvement are underway. For example, elimination of the need for recovery and recycle of either hydrogen chloride or fluorine would be of considerable economic advantage. With this in mind, experiments were conducted using once-through fluorine at low flow rates during the final stages of uranium recovery. At these low flow rates, the bed was not fluidized. High uranium recovery was achieved and the bed remained free-flowing. Fluorine requirements were only 6 grams per gram of uranium processed. Optimization of the hydrochlorination step so as to achieve maximum utilization of hydrogen chloride is also under investigation, both experimentally and by means of analog computer process simulation. Results of pilot plant runs, discussed below, indicate that hydrogen chloride utilization is more efficient as the scale of operation increases. Thus, on a plant scale, HCl recycle may not be economically warranted.

Installation of the pilot plant facility has been completed, and several runs have been made to test the equipment through the hydrochlorination step. (Figure II-3 is a photograph of the nearly completed pilot plant, prior to installation of the thermal insulation.) Nonirradiated multiplate assemblies of zirconium or aluminum without uranium were used in these experiments. These runs have provided operating experience and useful hydrochlorination rate data for future experiments. Acceptable reaction rates and HCl utilization efficiencies were demonstrated. The overall reaction rates averaged about 1.6 kg/hr for aluminum and 2.4 kg/hr for zirconium. Hydrogen chloride utilization efficiencies ranged between 45 and 56% for both metals. For assemblies of about 13 kg, the time required for complete reaction was as low as 6.4 hr for aluminum and 5.0 hr for zirconium. Figure II-4 shows an MTR-type, aluminum fuel assembly, similar to those processed, being loaded into the halogenation-fluorination reactor.

*Strontium (as SrCO_3), yttrium, niobium, molybdenum, ruthenium, rhodium (as RhCl_3), antimony, tellurium, cesium (as CsCl), barium (as BaCO_3), and cerium.

Figure II-3

PILOT PLANT FOR STUDY OF VOLATILITY PRO-
CESSING OF NONIRRADIATED HIGH ENRICHMENT
URANIUM ALLOY FUELS

(The pilot plant is nearly completed; the insulation has not yet been installed.)

Figure II-4

NONIRRADIATED MTR-TYPE FUEL ASSEMBLY BEING
LOADED INTO PILOT PLANT HALOGENATION-
FLUORINATION REACTOR

Operation of the fluid-bed pyrohydrolysis reactor (see Figure II-1), which is used to convert the volatile zirconium and aluminum chlorides to their respective oxides for greater ease of disposal, was conducted simultaneously with the hydrochlorination reactor. The conversion of the chlorides to oxides was about 96 to 99% complete. The remainder of the chlorides was present in the oxide product, probably as nonvolatile oxychlorides. It has not been determined that this chloride level will be detrimental to waste disposal, but efforts are being made to improve the conversion to oxide.

Operation of the pilot plant facility revealed a number of mechanical problems, mostly of a minor nature. It is believed that all of the problems encountered thus far have been overcome. Work with uranium-containing fuel materials is expected to start in the very near future.

A corrosion program designed to evaluate the suitability of nickel as a material of construction for equipment to be used in fluid-bed volatility processes is in progress. Corrosion tests are being made in which welded and nonwelded specimens are exposed in tube reactors to conditions of temperature, gas atmospheres, and gas cycling similar to those encountered under process conditions. Preliminary results have indicated very low corrosion rates (about 2 mils per year) for alternating exposures to atmospheres of hydrogen chloride and fluorine; however, the conditions of these tests are probably less severe than actual process conditions owing to the absence of the erosive action of the fluidized bed, absence of thermal cycling, and other factors. Other corrosion data is being obtained by exposure of corrosion specimens to processing conditions in the pilot plant equipment.

2. Processing of Nuclear Reactor Fuel of Low Enrichment

The current development program investigating the application of volatility processes to low enrichment fuels is concentrated on the processing of ceramic fuels of the type being used for commercial power reactors. At present, these fuels are made mainly from high density uranium dioxide pellets which are clad with either Zircaloy or stainless steel. Such fuels are frequently in the form of long tubular elements which are assembled into bundles containing several fuel elements, along with spacers and end fittings. The irradiated uranium fuels from central station power reactors will contain an appreciable percentage of plutonium, which also must be recovered because of its high economic value.

The major steps in the fluid-bed fluoride volatility process under development for fuels of this type are: decladding, fluorination, distillation, and reconversion to oxides. The conceptual process for a simple fuel composed of Zircaloy-clad uranium dioxide is briefly as follows: The fuel elements, after mechanical removal of extraneous hardware, are immersed in a bed of fluidized, high-fired granular alumina. The fuel jacket is removed by reaction with hydrogen chloride gas to convert the jacket to volatile zirconium tetra-

chloride which is removed and discarded as waste. The bare irradiated fuel pellets remain in the fluidized bed and are next exposed to fluorine gas at elevated temperature, about 500 °C, to convert the fuel material to volatile UF_6 and PuF_6 . Most of the fission products remain in the alumina bed and are discarded with the bed material as solid waste. The UF_6 and PuF_6 are fed to a distillation column for removal of the remaining fission products and for separation into two fractions, one composed of pure UF_6 , and the other composed of a mixture of PuF_6 and UF_6 . The latter fraction is then reconverted to oxides by reaction with a mixture of steam and hydrogen in another fluidized-bed reaction vessel. The final products are pure UF_6 and a granular form of mixed $\text{PuO}_2\text{-UO}_2$. This description of the process includes only the major process operations. The conceptual flowsheet is illustrated in Figure II-5, and the individual steps are discussed in greater detail in the following paragraphs.

Figure II-5

CONCEPTUAL FLOWSHEET FOR A FLUID-BED FLUORIDE VOLATILITY PROCESS

a. Separation of Fuel from Cladding

One method of separating the fuel from the cladding material is by chemical conversion of the cladding into a volatile compound. In the case of Zircaloy or aluminum claddings, this is readily accomplished by reaction with gaseous hydrogen chloride, the operation being virtually identical to that which has been demonstrated for enriched uranium alloy fuels. The evolved metal chlorides are converted to oxides by reaction with steam in a separate fluidized-bed reaction vessel and stored as wastes.

The chemical decladding of stainless steel-clad fuels is less fully developed. Stainless steel is not readily attacked by fluorine. In the past, gas-phase chlorination of the stainless steel was attempted, but corrosion was severe and interaction of the chlorine with the UO_2 caused difficulties owing to the production of a low melting oxychloride. A new approach has

been taken in recent bench-scale studies. This technique involves the introduction of liquid hydrochloric acid into a fluidized bed of alumina particles in which the clad fuel is submerged. With the bed temperature maintained at approximately 90 °C, the acid-moistened, fluidized bed attacks the stainless steel at rates which are dependent upon the amount of liquid acid in the bed. The work on this approach is preliminary, but the results are encouraging.

Studies have also been carried out on "oxidative decladding" procedures, in which the uranium dioxide is separated from the cladding by oxidation to U_3O_8 . The fuel tubes must first be broached by a mechanical method to expose the uranium dioxide. Oxidation results in chemical pulverization of the fuel, which permits separation of the finely powdered U_3O_8 from the metal cladding. Experiments were conducted to determine whether quantitative separation could be achieved for segments of chopped or sheared fuel elements, simulated by inserting dense UO_2 pellets into close-fitting stainless steel tubing of about 1/2-in. dia. by 1-in. length. The investigation was performed with the goal of incorporating such an operation into the two-zone, oxidation-fluorination scheme described below. The fuel tube segments were charged into a 2-in. dia. fluid-bed reactor to form a randomly packed (fixed) bed, and granular alumina was fluidized in the voids of the packed bed. The bed, while fluidized with nitrogen, was heated to 400 to 500 °C. At reaction temperature, the nitrogen was replaced by air.

It was found that uranium oxide removal from the cladding ceased after 60 to 80% had been separated. The volume increase resulting from the oxidation caused bulging of the cladding and compression of the uranium oxide, preventing its complete removal. The separation was improved, however, by any of the following methods:

- (1) gas-pulsing of the bed to provide some agitation of the fuel pieces,
- (2) reduction-reoxidation of the U_3O_8 residues, and
- (3) mechanical vibration of the bed.

The third method was the most effective. Internal vibration applied through a transmittance rod extending into the bed was more effective than external vibration from an electric vibrator. Under the best conditions, over 95% of the uranium oxide was separated from the cladding. It was concluded that quantitative separation could probably be achieved with adequate agitation of the fuel segments; however, it appeared that complex mechanical devices would be necessary.

An alternative procedure for separation of fuel from stainless steel cladding has recently been investigated. This procedure involves puncturing the cladding mechanically to provide a row of small perforations along the length of the tube. The element is then exposed to an atmosphere of oxygen mixed with nitrogen at a temperature of about 450 °C. The encased uranium dioxide reacts with the oxygen, producing U_3O_8 . This chemical conversion

creates large internal stresses caused by the differences in densities of the two oxides and results in the rupturing of the tubing along the row of perforations. The uranium oxide is thus discharged from the stainless steel tube in the form of finely divided particles of U_3O_8 . This method of oxidative de-cladding can be combined with the fluorination step so that both operations are conducted simultaneously in the same vessel, as explained below. The decladding procedure has been successfully demonstrated on an engineering scale with simulated fuel elements; virtually complete removals of UO_2 were achieved. A number of mechanical problems remain to be solved, particularly the development of suitable means for puncturing the fuel tubes.

b. Fluorination of Uranium Oxide

When the cladding is removed from the fuel elements by chemical methods, as in the case of Zircaloy cladding, the exposed uranium dioxide fuel material will be in the form of pellets or similar massive pieces. Techniques for conversion of this material into uranium and plutonium hexafluorides are under study.

During the past year, work has been directed toward evaluation of the batch-fluorination of uranium dioxide pellets by a two-zone technique, wherein oxygen and nitrogen are introduced into the lower reaction zone (oxidation zone) formed by the uranium dioxide pellet bed, and fluorine is introduced above the pellets into the upper zone (fluorination zone), which consists of fluidized alumina. The alumina is also fluidized below the pellet support plate, and in the voids of the pellet bed by the oxygen-nitrogen mixture. Temperatures in the pellet zone are sufficiently high ($\sim 375^\circ\text{C}$) to ensure the formation of U_3O_8 fines rather than nonstoichiometric intermediate uranium oxides. The U_3O_8 fines ($\sim 20\mu$ diameter) are of high specific surface area and, consequently, are highly reactive. These fines are formed in the lower zone of the reactor by oxidation and are transported to the upper zone where they are contacted with fluorine and removed as uranium hexafluoride in the gas phase. This separation of the oxidation and fluorination reactions into two distinct steps results in several advantages. The undesirable caking tendencies which exist when both reactions occur simultaneously in the same zone are avoided. The quality of fluidization in the upper zone is improved by the absence of pellets and heat removal is more favorable than in single-zone oxidation-fluorination. This latter improvement arises from the fact that the oxidation of uranium dioxide to U_3O_8 fines ($\Delta H = -26$ kcal/gram mole uranium at 25°C) takes place in the pellet bed in which fluidization is hindered by the pellets, and the fluorination of the uranium fines ($\Delta H = -231$ kcal/gram mole uranium at 25°C) takes place in the unhindered, upper fluid bed, which has substantially higher rates of heat transfer than the pellet zone.

The arrangement of the experimental equipment is shown in the diagram of Figure II-6. The nickel fluidized-bed reactor is 3 in. in diameter by 4 1/2 ft long; an enlarged disengaging section surmounts the reaction section

Figure II-6

SCHEMATIC DIAGRAM OF EQUIPMENT FOR TWO-ZONE
OXIDATION-FLUORINATION OF URANIUM DIOXIDE
PELLETS

and houses the two process gas filters. Automatic, periodic blowback of the sintered nickel filters is provided by means of reverse gas flow through gas compressor jets located in the downstream line of each filter. Heating of the reactor is done by electric tubular heaters bonded to the reactor wall by a copper metallizing technique. Cooling is provided by passing air (maximum flow of 400 cfm) through a finned annulus around the outside of the reactor. Uranium hexafluoride is collected in a 10-ft long, 3-in. diameter nickel condenser cooled by trichloroethylene, which is circulated through a refrigeration unit. The condenser is equipped with flexible lines and mounted on a remote-reading scale in order to monitor collection rate by weight change. A sodium fluoride adsorber is also provided to complete the removal of UF_6 from the gas stream.

To promote mixing and transport of the U_3O_8 fines, the fluid bed is pulsed. Pulse nitrogen is introduced to the column immediately below the pellet support plate. At the minimum pulse duration of 0.04 sec., approximately 0.02 cu ft of nitrogen is admitted to the column with each pulse. Fluorine, oxygen, and nitrogen flow rates are controlled manually or automatically by a system of orifices and flow control valves. Once-through gas flow is maintained until most of the uranium dioxide pellet bed has been reacted, after which the gas system is put on recycle (a Lapp diaphragm compressor is used) to complete the removal of uranium compounds from the alumina bed. Recycle offers a means of increasing fluorine economy. Fluorine concentration in the reactor off-gas is monitored by passing a

portion of the gas through a sodium chloride trap; the resulting reaction replaces fluorine with chlorine in the sample gas, and the chlorine is analyzed continuously by thermal conductivity.

Experimental results showed that the rate of pellet oxidation exhibited a first-order dependence upon oxygen concentration and was also temperature dependent, with rapid rates at 500°C and above. The fluorination reaction was also shown to be quite rapid and increased with temperature. The major development required for successful operation at practical hexafluoride production rates was control over the transport of the finely divided U_3O_8 from the oxidation zone. Adequate control of fines transport implied that no accumulation of U_3O_8 fines would occur in the oxidation zone, thereby reducing the possibility of slug flow of these fines to the fluorination zone. Slug flow of the fines results in intermediate uranium fluoride formation and elutriation of fines to cooler parts of the reactor. The several methods of promoting fines transport which were investigated included increased fluidization gas velocities, column vibration, longitudinal pellet bed temperature gradients, and the use of pulsed gas introduced to the fluidized-packed bed.

The effectiveness of the methods used to promote fines transport may be compared by means of the data shown in Table II-1, in which the results of a series of two-zone runs are summarized. Since temperature control and freedom from caking were achieved by use of the two-zone oxidation-fluorination technique, data evaluation was based upon the overall rate of UF_6 production and the overall fluorine efficiency for a run. The goal of the experimental runs was to achieve an overall production rate of 50 lb UF_6 / (hr) (sq ft) and an overall fluorine efficiency of 75%.

Runs 61 and 64 indicated that the use of column vibration and thermal gradients in the pellet bed was satisfactory for production rates of about 30 lb UF_6 / (hr)(sq ft) and fluorine efficiencies in the range 50 to 60%. In Runs 65 and 67, plugging of the fluorine inlet line occurred, which indicated a sudden and excessive increase in the quantity of U_3O_8 fines in the fluorination zone. In Run 66, the entire batch of pellets was oxidized; however, only 56% of the charge was converted to the hexafluoride, and the remainder was collected as U_3O_8 and intermediate uranium fluorides in the column disengaging section. These results indicated that the rates of U_3O_8 formation were too high. In Runs 68 to 70, in which gas pulsing and lowered oxygen concentrations of 4.5 to 8.0% were used, effective control of the rate of U_3O_8 fines formation and transport to the oxidation zone was achieved, together with high UF_6 production rates and fluorine utilization. Optimization of the reaction conditions was achieved in the last two runs in which 6 to 8% oxygen was used. The desired production rate of 50 lb UF_6 / (hr)(sq ft) and the desired fluorine efficiency of 75% were obtained.

Table II-1
TWO-ZONE OXIDATION-FLUORINATION OF UO_2 PELLETS

UO ₂ pellet charge:	Weight:	19.4 lb
	Bed height:	12 in.
Alumina charge:	Weight:	11.9 to 17.8 lb
	Size limits:	-40 +170 mesh
Oxygen diluent:	Nitrogen	
Fluorine diluent:	Runs 61-67:	None
	Runs 68-70:	Process off-gas

Run No.	Mode of Operation	Oxidation Zone			Fluorination Zone			UO ₂ Process Reacted		Average Production Rate [lb UF ₆ / (hr)(sq ft)]	Average Fluorine Utilization Efficiency ^a (%)
		Temp (°C)	Oxygen (%)	Gas Rate (cfm)	Temp (°C)	Fluorine (%)	Gas Rate (cfm)	Time (hr)	to UF ₆ (%)		
61	Intermittent Column Vibration	500	3 to 8	1.4	500	13	1.6	15.5	88	32.0	58.6
62	Continuous Column Vibration	400	4 to 12.5	1.3	500	13	1.4	13.0	82	32.4	53.6
63	Thermal Gradients ^b	400	18 to 31	1.1	525	15	1.3	13.8	95	35.6	49.0
64	Thermal Gradients ^b	400	26	1.2	525	11	1.3	16.3	97	31.0	53.0
65	Thermal Gradients ^b	400	23	1.3	500	12	1.4	7.5	25	20.4	48.0
66	Pulsed Gas	400	22	1.3	500	7	1.4	13.5	46	17.6	49.5
67	Pulsed Gas	400	20	1.0	500	11	1.1	1.5	-	-	-
68	Pulsed Gas	400	4.5	0.9	500	14	1.3	13.5	100	37.9	66.5
69	Pulsed Gas	400	6	0.9	500	15	1.4	10.0	100	50.0	74.9
70	Pulsed Gas	400	8	1.0	500	12	1.4	9.2	100	52.0	78.5

^a Avg. fluorine utilization efficiency = $100 \left[\frac{3 \text{ (mole UF}_6 \text{ produced)}}{\text{mole F}_2 \text{ fed}} \right]$

^b The temperature of the UO₂ pellet bed was lower at the bottom, in order to promote oxidation preferentially near the upper surface of the bed.

Other runs were then conducted in an effort to combine the oxidative decladding step with the fluorination step in a single vessel. In several runs, 1-in. long segments of stainless steel tubing, each containing two uranium dioxide pellets, were used to simulate fuel elements which had been chopped or sheared. The results of these runs showed that most of the uranium was separated from the stainless steel segments and fluorinated to UF_6 in the fluorination zone. However, about 20 to 30% of the uranium oxide remained lodged in the tubes, necessitating the introduction of fluorine into the lower (oxidation) zone in order to convert this uranium oxide to UF_6 . Although acceptable results were achieved, the rate of conversion to UF_6 was not as high as desired.

Much better results were obtained using 10 to 12-in. long sections of stainless steel tubing which were either slit or perforated longitudinally. Both 10-mil and 20-mil thick wall tubing containing UO_2 pellets were used. These were charged into the oxidation zone of the reaction vessel and operations conducted as outlined above. The fuel tubes ruptured allowing the pulverized U_3O_8 to be transported completely to the fluorination zone of the reaction vessel. In a typical experiment, a batch of twelve 12-in. long stainless steel tubes containing 3200 g of UO_2 pellets was processed in the 3-in. diameter reactor. The fuel material was completely separated from the cladding and was 96% converted to UF_6 in 7.5 hr of operation at a fluorination temperature of 475°C. The efficiency of utilization of the inlet fluorine gas was 72%.

The results obtained in these experiments indicate that separation and recovery of uranium as hexafluoride from stainless steel-clad UO_2 fuel elements can be achieved, provided that the mechanical pretreatment (chopping, slitting, or perforating) can be practically and economically carried out. Because of the uncertainty about the economics of the mechanical operations, the attempt to develop a chemical decladding step compatible with the fluid-bed fluorination approach will be continued.

Supporting studies have been continued of the basic behavior of fluidized-packed bed systems for the purpose of assisting in the design and interpretation of process equipment operation. Previously, heat transfer studies had established typical values of effective thermal conductivity in both the lateral and vertical directions. Lateral heat conduction studies have now been extended to include various sizes of fixed packing, various sizes and types of fluidized particles, two fluidizing gases, and a range of gas velocities. This work has resulted in a simple mathematical correlation which appears to be generally applicable to all conditions of interest. The correlation relates the thermal diffusivity to the diameter of the fixed packing, the gas velocity, and the minimum fluidization velocity. It is thus possible to calculate the effective thermal conductivity from the easily measured properties of the system.

Because the two-zone, oxidation-fluorination scheme depends upon the transport of fine U_3O_8 particles from the oxidation zone to the fluorination

zone, a study was carried out to investigate the factors which affect the longitudinal (axial) movement of particulate solids in fluidized-packed bed reactors. Fine nickel powder and copper shot were used, together with metal spherical packing, to simulate the process system. Mixing diffusion coefficients were obtained for both the fluidized copper shot system and for the transport of the nickel fines in the bed of copper shot. The rate of fines transport was found to be about one to two orders of magnitude greater than the solids movement of the coarser fluidized particles. Representative values of the fines transport diffusivity obtained in this experimental study should be useful in estimating the maximum practical oxidation rate for design purposes. To avoid accumulation of oxide fines in the lower (oxidation) zone of a two-zone reactor, the oxidation rate should not be allowed to exceed the fines transport rate.

In addition to the above studies, work has been completed on several other studies which were conducted to support the process development or to aid in the design of fluid-bed reactors. These include investigations of (1) lateral solids mixing in fluidized-packed beds, (2) radial gas mixing in fluidized-packed beds, and (3) effects of solid thermal properties on heat transfer to gas-fluidized beds. Since the results of this work constitute worthwhile additions to the fluidization literature, papers have been prepared and submitted to appropriate technical journals for publication.

c. Engineering-scale Plutonium-handling Facility for Fluoride Volatility Studies

The first phase of construction of an engineering-scale alpha facility to study various steps of the fluoride volatility processes for low enrichment, plutonium-bearing fuels has been completed. This phase of construction includes the 3-in. dia. fluorination unit and its auxiliaries, such as condensers, refrigeration system, chemical traps, process gas scrubber, and gas filtration equipment. The presence of volatile plutonium hexafluoride in this processing scheme has necessitated extra precautions in the design of the containment systems. The equipment is housed in two large alpha-containment boxes having an elaborate system for ventilation and for scrubbing and filtration of the ventilation gas. The main alpha-box is located in a concrete cell which is separately ventilated.

Some of the features of this facility are shown in Figures II-7, II-8, and II-9. Figure II-7 illustrates the general layout of the facility. Figure II-8 shows the fluorination reactor mounted in the large alpha-box, prior to installation of piping and insulation. Figure II-9 illustrates the instrument panelboard and the top of the small alpha-box, showing the large bag-out ports for equipment removal.

Testing of the process equipment is in progress. A number of experiments will be conducted using uranium dioxide without plutonium.

Figure II-7

ENGINEERING-SCALE PLUTONIUM HANDLING FACILITY FOR FLUORIDE VOLATILITY REPROCESSING STUDIES

Initial runs will be made without the windows and glove ports of the containment boxes in place. After final testing of the system, the boxes will be sealed and experiments made with UO_2 - PuO_2 fuel material.

The second phase of construction of the engineering-scale facility will include a system for the conversion of mixtures of UF_6 and PuF_6 to the more stable oxide form by reaction with steam and hydrogen in a fluidized bed. The technology for performing this operation in a fluidized-bed reactor has been developed for UF_6 , but not for mixtures of UF_6 and PuF_6 . The behavior of the mixed hexafluorides is expected to be similar to that of UF_6 . Installation of the converter reactor is important because of the difficulty of storing the mixed hexafluoride products which will be obtained from the fluorinator. Conversion of this material to oxides will also allow its re-use in certain fluorination experiments in which the pelletized form of the

mixed oxides is not essential. This is important because of the very high cost of UO_2 - PuO_2 pellets at the present time. Installation of the converter system is, therefore, being carried out while the testing of the fluorinator is in progress.

The third phase of construction will include other components needed for complete demonstration of the process flowsheet. These components may include decladding equipment and hexafluoride distillation equipment. Plans for this phase are not yet firm.

d. Separation of Plutonium Hexafluoride from Contaminated Exhaust Air

Glove box enclosures used for handling plutonium and its compounds are equipped with high efficiency (AEC) filters to prevent the escape of particulate plutonium. Release of pure plutonium hexafluoride or uranium hexafluoride into moist air results in rapid reaction with the available water to produce a solid reaction product (PuO_2F_2 or UO_2F_2), which is efficiently removed by the filters.

Figure II-8

REACTOR FOR STUDYING THE FLUORINATION
OF UO_2 - PuO_2 FUEL MATERIALS

Previously reported work (see ANL-6766, pp. 87-88) in which small quantities (1 to 25 mg) of pure PuF_6 were released into air of controlled humidity indicated that the hydrolysis reaction rapidly went to completion in the gas phase to produce a gas suspension of small solid particles (smoke). When there was sufficient moisture in the air to hydrolyze completely the PuF_6 released, the penetration of two AEC filters in series varied from one part per million to two parts per billion.

To evaluate quantitatively the extent to which small quantities of unhydrolyzed material may contribute to total filter penetration, exploratory hydrolysis experiments have been made with uranium hexafluoride. The hydrolysis behavior of UF_6 is important for the general air clean-up problem in work with UF_6 - PuF_6 mixtures. Moreover, it is believed that the mechanisms

Figure II-9

INSTRUMENT PANELBOARD AND PORTION OF
TOP OF SMALL ALPHA-BOX

of hydrolysis for these hexafluorides are sufficiently similar that the results of the UF_6 experiments will be useful in designing subsequent PuF_6 experiments. The present UF_6 experiments, described below, indicate that, when the hexafluoride vapor is diluted with dry nitrogen before being mixed with humidified nitrogen, the gas phase reaction is not rapid and most of the reaction takes place on solid surfaces. This is an important effect to be taken into account in designing an effective practical method for clean-up of PuF_6 released into cell exhaust air.

The hydrolysis reaction in the present series of experiments was studied in a Plexiglas tube 1.5 in. in diameter by 51.5 in. long. Two gas streams of equal volumetric flow rate containing a known partial pressure of UF_6 and H_2O entered one end of the tube. The reactants were mixed by diffusion while flowing down the tube and passed through a filter mounted across the discharge end of the tube. The results of the filter penetration measurements are reported in Table II-2. The high penetrations reported result from incomplete reaction in the gas phase before the filter.

Table II-2

GAS-PHASE HYDROLYSIS AND FILTRATION OF URANIUM HEXAFLUORIDE

Reaction time before filter:	14.5 sec.
Filter media:	AEC "Absolute" Type
Diluent gas:	Nitrogen
Total superficial gas velocity (1 atm, 25°C):	9.7 cm/sec

Run No.	Partial Pressure ^a (mm Hg)		Filter Penetration ^b (%)
	UF ₆	H ₂ O	
1	0.005	0.08	19
2	0.06	0.09	28
3	0.005	0.8	15
4	0.005	7.6	1

^a These partial pressures apply to the separate reagent streams. In the combined (mixed) streams, the values are one-half those shown in the table.

^b Percent of uranium incident on filter that passed through filter.

Subsequent experiments, in which dilute mixtures of UF₆ and water vapor were passed through beds of glass beads of known surface area, indicate that the reaction is largely heterogeneous and catalyzed by solid surfaces. This would imply that the reaction is catalyzed by its own solid product, thus accounting for the rapid hydrolysis previously observed. However, for very dilute mixtures of UF₆ in air or nitrogen, as in the present experiments, the amount of solid product in the gas phase is probably not sufficient to be significant. Work is continuing with UF₆ and PuF₆ on the measurement of reaction kinetics using packed beds of known surface area. Equipment is also being installed for the study of surface reaction kinetics using plutonium hexafluoride. This equipment is being set up in a new plutonium glove box facility.

B. Laboratory Investigations of Fluoride Volatility Processes

Laboratory studies were continued in support of the program for the development of fluoride volatility processes for the recovery and purification of nuclear reactor fuels. Experiments were conducted in an effort to devise a fluorination scheme whereby optimum removals of uranium and plutonium could be achieved from refractory alumina used in fluid beds, since the alumina will be discarded as waste after use. Studies of the effect of alpha and gamma radiation on PuF₆ were also continued. The use of the absorption spectrum of PuF₆ as a means of determining the amounts of PuF₆ present in PuF₆-UF₆

mixtures was investigated. Equipment is now being built to study the liquid-vapor and solid-liquid phase equilibria for systems involving plutonium fluorides and uranium fluorides. A program of study of the chemistry of neptunium hexafluoride has been initiated.

1. Removal of Plutonium and Uranium as Hexafluorides from Fluidized Beds of Alumina by Fluorination

Laboratory studies are being made of the fluid-bed fluorination of U_3O_8 - PuO_2 mixtures. This work is a continuation of the fluorination work in which the removal of plutonium and uranium from inert solids in static beds was studied (see ANL-6766, p. 82). The present work is being carried out to further substantiate the flowsheet and to determine the proper operating conditions for the pilot plant, described in the previous section, for the processing of nuclear reactor fuels of low enrichment. The work is directed toward determining the reaction conditions and procedures which would result in a high degree of removal of uranium and plutonium as hexafluorides from the alumina fluid bed. Mixtures of U_3O_8 and PuO_2 are being used in this work to represent the product which is formed by the oxidation of UO_2 - PuO_2 fuel pellets. The U_3O_8 - PuO_2 powder, mixed with alumina, is carried into the fluid bed of alumina in a fluidizing nitrogen stream at a rate of 1 to 5 g of U_3O_8 - PuO_2 per minute. Fluorine is brought into the bed just above the point at which the U_3O_8 - PuO_2 powder enters the fluid bed and the fluorination reaction occurs as the reactants mix. This scheme simulates the condition encountered in the upper (fluorination) zone of the two-zone procedure.

This report presents the results of initial fluid-bed fluorination experiments. The aims of these and future experiments are to evaluate the following: (1) the level of plutonium retention in the alumina bed under various reaction conditions, (2) the relative rates of fluorination of U_3O_8 and PuO_2 , (3) comparison of fluorination rates of U_3O_8 - PuO_2 mixtures prepared by the oxidation of UO_2 - PuO_2 solid solutions with those of mixtures prepared by mechanically mixing U_3O_8 and PuO_2 .

The fluid-bed apparatus being used in this work is similar to that used for the fluorination of U_3O_8 . A schematic diagram of the apparatus is shown in Figure II-10. The apparatus consists of the following major components: (1) a 1 1/2-in. diameter fluid-bed fluorinator, (2) a powder feeder, (3) a system of cold traps used to condense the UF_6 - PuF_6 product, (4) a Lapp diaphragm pump employing a remote head, which circulates the gas phase, (5) activated alumina traps for the disposal of fluorine, and (6) manifolds supplying fluorine, nitrogen, and vacuum service. All of the apparatus is contained within an alpha glove box and manipulation of the apparatus is accomplished through glove ports. The alpha glove box, details of which

Figure II-10

FLUID-BED FLUORINATION REACTOR

have been published,⁴ was three modules in length and 1 1/2 modules in height. (A module is a cube 40 inches on edge.) Figure II-11 is a photograph of one face of the alpha box showing the placement of the apparatus before all of the windows and gloves had been put in place. Figure II-12 shows a close-up view of the fluid-bed reactor.

Mixtures of U_3O_8 and PuO_2 , containing about 0.4 w/o plutonium, were prepared either by adding commercially produced U_3O_8 to the product obtained by oxidizing pellets of UO_2 - PuO_2 solid solution which contained about 4 w/o plutonium or by blending U_3O_8 and PuO_2 . To some of the mixtures of U_3O_8 and PuO_2 , a mixture of 11 fission product element oxides was added. The fission product oxide concentration in the mixture was 0.86 w/o.

Commercial grade fluorine, which was passed through a sodium fluoride trap at 100 C to remove HF, was used. The nitrogen, which was used as the fluidizing gas and also as a diluent for the fluorine, was passed through a trap containing molecular sieves to remove water. High-purity fused alumina was employed as the inert fluidized material.

The fluorinations of the U_3O_8 - PuO_2 mixtures were performed using two reaction periods. In the first period, which will be referred to as the feeding-fluorination period, the U_3O_8 - PuO_2 powder was injected into the fluid bed and reacted with fluorine. The fluorine, which was 20 v/o of the total flow, was diluted with an equal quantity of nitrogen before it entered the bed. The U_3O_8 - PuO_2 -alumina mixture was introduced at a rate of from one to five grams of U_3O_8 - PuO_2 mixture per minute into the fluidizing nitrogen stream and then into the fluid bed, at a point below the fluorine inlet (see Figure II-10). The gas velocity in the 3/8-in. diameter fluidizing nitrogen inlet line into which the U_3O_8 - PuO_2 mixture was fed was five feet per second. Total flow rate through the fluid bed was 12 liters per minute, with the fluidizing nitrogen contributing approximately seven liters per minute and the mixture of fluorine and nitrogen contributing approximately five liters per minute. The superficial

⁴Malecha, R. F., H.O. Smith, J. H. Schraidt, J. V. Natale, N. E. Ross, and H. L. Brown, Jr., "Low Cost Gloveboxes", Proceedings of the Eighth Conference on Hot Laboratories and Equipment, TID-7599, 485-493 (1960).

Figure II-11

EQUIPMENT FOR STUDY OF FLUID-BED FLUORINATION
OF U_3O_8 - PuO_2 MIXTURES

velocity in the fluid bed was about 0.6 ft/sec at room temperature (about 1.5 ft/sec at 500°C). During the feeding-fluorination period, performed at 450 or 500°C, about 99% of the uranium was converted to UF_6 and part of the plutonium, between 40 and 70 w/o, was converted to PuF_6 . In the second period, which will be referred to as the recycle-fluorination period, the fluorine content at the inlet to the fluid bed was raised to about 100%, and the gas was cycled by the Lapp pump at a flow rate of 8 liters/min and returned to the fluidized bed. This recycle-fluorination period was intended to remove essentially all of the remaining uranium and plutonium, and was performed at either 500 or 550°C. After the completion of the reaction, the cold traps were evacuated, then warmed to room temperature, and weighed to obtain the amount of UF_6 and PuF_6 collected. The alumina, which was used as the fluid bed medium, was removed from the reactor and samples were taken for uranium and plutonium analyses. The small amount (about 1 to 2 grams) of a mixture of U_3O_8 - PuO_2 and alumina which was retained in the disengaging section was removed and submitted for uranium and plutonium analyses.

Preliminary experiments, with U_3O_8 alone, were first made to

Figure II-12

BENCH-SCALE FLUID-BED REACTOR FOR
STUDY OF FLUORINATION OF U_3O_8 - PuO_2
MIXTURES

determine the efficiency of the cold traps for collections of UF_6 . Nine experiments were performed in which the feeding-fluorination period at $500^\circ C$, using 20 v/o fluorine, was followed by a recycle-fluorination period of five hours at $500^\circ C$, using 100% fluorine. The average results for these experiments showed a conversion of $99.7 \pm 0.1\%$ of the U_3O_8 to UF_6 and a cold trapping efficiency of 99.3%.

The results of the experiments of the fluorination of U_3O_8 - PuO_2 mixtures are listed in Table II-3. In all the experiments, the feeding-fluorination period was performed at $500^\circ C$, employing 20 v/o fluorine in nitrogen. The results of the experiments in which the U_3O_8 - PuO_2 used did not contain fission product oxides are listed in the first part of Table II-3; the results of

the experiments in which fission products were present are listed in the second part of the table.

Table II-3

FLUORINATION OF U_3O_8 - PuO_2 MIXTURESExperimental Conditions

Feeding-Fluorination Period:

Bed temperature:	500° C
Total gas flow:	12 liters/min
F ₂ concentration:	20 v/o
Alumina in bed:	400 g
Alumina in feed:	150 g
U ₃ O ₈ -PuO ₂ feed:	300 g
U ₃ O ₈ -PuO ₂ feed rate:	1 to 5 g/min

Recycle-Fluorination Period:

Total gas flow:	8 liters/min
F ₂ concentration:	100%

Recycle-Fluorination
PeriodConcentration in
Al₂O₃ Bed after Fluorination

Temp (°C)	Time (hr)	w/o U	wt. U (g)	w/o Pu	wt. Pu (g)
Part 1, No fission products present. ^a					
500	5	0.021	0.120	0.033	0.187
550	5	0.003	0.016	0.022	0.124
500	15	0.007	0.041	0.030	0.157
550	15	0.014	0.075	0.011	0.056

Part 2, Fission products present.^b

500	5	0.016	0.069	0.057	0.330
550	5	0.017	0.096	0.038	0.220
550	15	0.021	0.117	0.029	0.165

^a U₃O₈-PuO₂ mixture contained 253 g U and 1.05 g Pu.

^b U₃O₈-PuO₂-F.P. mixture contained 241 g U, 1.13 g Pu and 2.58 g of a mixture of fission product oxides containing the following oxides: La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Y₂O₃, BaO, ZrO₂, and MoO₃.

In the experiments in which fission product oxides (F.P.) were present, the concentrations of uranium and plutonium on the alumina were 0.016 w/o uranium and 0.057 w/o plutonium after five hours of fluorination at 500° C, and 0.017 w/o uranium and 0.038 w/o plutonium after five hours of fluorination at 550° C. After 15 hours of recycle-fluorination at 550° C, the uranium and plutonium concentrations on the alumina bed were 0.021 w/o and 0.029 w/o, respectively.

In an experiment in which only the initial feeding-fluorination period was carried out, the alumina bed contained 0.149 w/o uranium and 0.106 w/o plutonium. These concentrations on the alumina correspond to 0.4% of the uranium and 56% of the plutonium fed to the reactor. This is indicative of the greater rate at which uranium is fluorinated relative to plutonium.

The presence of fission product oxides in the U_3O_8 - PuO_2 mixtures did not materially increase the uranium retention on the alumina; in all cases the quantities of uranium retained represented less than one percent of those fed to the reactor. The presence of fission products in the U_3O_8 - PuO_2 mixture did, however, result in a substantial increase in the plutonium retention on the alumina.

A series of experiments were performed using a lower temperature, 450° C, during the feeding-fluorination period and during a five-hour recycle-fluorination period. These two periods at 450° C were followed by recycle-fluorinations of five hours at 500° C and 10 hours at 550° C. The fluorine concentration was 20 v/o during the feeding-fluorination period and 100% during the recycle-fluorination period. These conditions were chosen to approximate those used in the previous boat experiments (ANL-6766, page 83, Table II-1). In the boat experiments, an initial reaction period, using a low temperature (450° C) and low fluorine concentration (10%), was followed by a reaction period at a higher temperature (550° C) and a higher fluorine concentration (75%). During the feeding-fluorination period in the present series of experiments, a mixture of 300 g of U_3O_8 - PuO_2 -F.P. and 150 g of alumina was fed into the reactor at a rate of between one and two grams per minute. Two types of U_3O_8 - PuO_2 -F.P. feed mixtures were used in these experiments. In one type of feed mixture, the PuO_2 was obtained by the oxidation of pellets of UO_2 - PuO_2 solid solution; the second type of feed mixture was prepared by mechanically mixing U_3O_8 and PuO_2 .

The results obtained in these experiments are listed in Table II-4. The results of three experiments in which the U_3O_8 - PuO_2 -F.P. mixtures contained about 0.4 w/o Pu showed a range of plutonium content of the alumina from 0.004 to 0.007 w/o. (In the boat experiments, which were performed under similar reaction conditions, the average residual concentration of plutonium on the alumina was 0.006 w/o.) The results of the fluid-bed fluorination experiments also indicate that the source of the PuO_2 (solid

solution or physical admixture) does not materially influence the retention of plutonium on the alumina. In the one experiment in which the U_3O_8 - PuO_2 -F.P. mixture contained about 3 w/o plutonium, the alumina bed after the reaction contained 0.14 w/o plutonium. This last result would seem to indicate that the residual plutonium content of the alumina bed is in some manner dependent on the quantity of plutonium fed to the reactor. An additional variable in this experiment was the increase in the content of fission product element oxides in proportion to the increase in plutonium content, which could also have a bearing on the larger plutonium content of the alumina bed.

Table II-4

FLUORINATION OF U_3O_8 - PuO_2 -FISSION PRODUCT MIXTURESExperimental Conditions

Feeding-Fluorination Period:

Temperature:	450° C
Total gas flow rate:	12 liters/min
F_2 concentration in total flow:	20 v/o
Alumina in bed:	400 g
Alumina in feed:	150 g

Recycle-Fluorination Period:

1st period:	450° C, 5 hr
2nd period:	500° C, 5 hr
3rd period:	550° C, 10 hr
Total gas flow rate:	8 liters/min
F_2 concentration:	100 percent

U_3O_8 - PuO_2 -F.P. Feed Mixture		U and Pu Concentration in Bed			
Feed Rate (g/min)	PuO_2 Source	w/o Pu	wt. Pu (g)	w/o U	wt. U (g)
1.95 ^a	Solid Solution	0.007	0.040	0.015	0.085
1.3 ^b	Physical Admixture	0.006	0.037	0.003	0.014
1.3 ^c	Physical Admixture	0.004	0.022	0.004	0.022
1.1 ^d	Physical Admixture	0.14	0.841	0.03	0.180

^a Feed Contained: 252 g U, 1.182 g Pu, 2.58 g F.P., 150 g Al_2O_3 .

^b Feed Contained: 252 g U, 1.580 g Pu, 2.58 g F.P., 150 g Al_2O_3 .

^c Feed Contained: 252 g U, 1.16 g Pu, 2.58 g F.P., 150 g Al_2O_3 .

^d Feed Contained: 216 g U, 9.00 g Pu, 19.4 g F.P., 150 g Al_2O_3 .

An experiment was also performed to investigate the effect on the plutonium concentration of an alumina bed when it was re-used for the fluorination of several batches of a U_3O_8 - PuO_2 mixture containing fission product oxides. In this experiment, six additions of 300 g of a U_3O_8 - PuO_2 -F.P. mixture were fed to the alumina bed during feeding-fluorination periods at $500^\circ C$; the six feeding-fluorination periods were followed by two recycle-fluorination periods of 10 hours each at $500^\circ C$ and $550^\circ C$. Each addition of 300 g of U_3O_8 - PuO_2 -F.P. mixture contained, on the average, 251.4 g U, 1.165 g Pu, and 2.58 g F.P. At the end of each feeding-fluorination period and recycle-fluorination period, the alumina bed was removed from the reactor and sampled for analysis. For each additional feeding-fluorination period, 400 g of the alumina bed from the previous run was replaced in the reactor and 150 g of the alumina bed was mixed with the next 300 g charge of U_3O_8 - PuO_2 -F.P. mixture. Table II-5 lists the experimental conditions used and the results obtained for this experiment. The plutonium content of the alumina bed was 0.10 w/o after the first addition, increased almost linearly to 0.30 w/o after the third addition, remained at that level after the fourth and fifth additions, and then dropped to 0.23 w/o after the sixth addition. The two recycle-fluorination periods did not materially reduce the plutonium content of the alumina bed, the concentrations being 0.19 and 0.18 w/o after the first and second recycle-fluorination periods, respectively. The uranium concentration in the alumina bed, which was 0.64 w/o after the sixth addition, was reduced to 0.03 w/o after the second recycle-fluorination period. The re-use of the alumina bed did not result in a lower overall retention of plutonium than would have resulted from six separate fluorination experiments of the type shown in the last entry in Table II-3 (i.e., feeding-fluorination period at $500^\circ C$, recycle-fluorination period of 15 hours at $550^\circ C$), in which the alumina bed contained 0.029 w/o plutonium. It is of interest to compare the result of the last experiment in Table II-5 with that of the last experiment listed in Table II-4, in which a U_3O_8 - PuO_2 -F.P. mixture containing 9 g of plutonium was fed into an alumina bed in one feeding-fluorination period. These two experiments resulted in about the same concentrations of plutonium on the alumina beds, 0.14 and 0.18 w/o.

Two experiments were performed in which only PuO_2 or PuO_2 -F.P. mixed with Al_2O_3 was fed into the fluid bed. The feeding-fluorination period was performed at $500^\circ C$ and this was followed by a recycle-fluorination period of ten hours at $550^\circ C$. In one experiment 1.3 g of PuO_2 was fluorinated; in the second experiment 1.3 g of PuO_2 and 2.6 g of fission product oxides were fluorinated. The fluid-bed alumina contained 0.008 w/o and 0.005 w/o plutonium for the PuO_2 only and the PuO_2 -fission product oxide experiments, respectively. These results show that in the absence of uranium the residual plutonium concentration on the alumina is not affected by the presence of fission products.

On the basis of the results obtained thus far in the fluid-bed fluorination study, the following general conclusions may be stated:

Table II-5

RECYCLE USE OF AN ALUMINA BED FOR SIX FLUORINATIONS
OF U_3O_8 - PuO_2 -FISSION PRODUCT MIXTURE

Experimental Conditions

Feeding-Fluorination Period:

Total gas flow rate:	12 liters/min
F_2 concentration:	20 v/o
Alumina in bed:	400 g
Alumina in feed:	150 g
U_3O_8 - PuO_2 -F.P.:	1800 g (in six batches of 300 g each)
U_3O_8 - PuO_2 -F.P. feed rate:	~5 g/min

Recycle-Fluorination Period:

Total gas flow rate:	8 liters/min
F_2 concentration:	100 percent

Bed Temp (°C)	Reaction Time (hr)	U and Pu Concentrations in Al ₂ O ₃ Bed			
		w/o U	wt U (g)	w/o Pu	wt Pu (g)
Feeding-Fluorination Periods ^a					
500	1	0.16	0.93	0.10	0.57
500	1	0.24	1.38	0.21	1.21
500	1	0.17	1.02	0.28	1.71
500	1	2.03	11.4	0.31	1.84
500	1	1.90	11.0	0.30	1.74
500	1	0.64	3.68	0.23	1.34
Recycle-Fluorination Periods					
500	10	0.13	0.71	0.19	1.06
550	10	0.01	0.05	0.18	0.92

^a Each of the six additions of U_3O_8 - PuO_2 -F.P. mixture contained an average of 251.5 g U, 1.165 g Pu, and 2.58 g F.P. The total quantities added were: 1508 g U, 6.98 g Pu, and 15.4 g F.P.

1. The results obtained in the fluid-bed study are similar to those obtained in the prior boat reactor experiments. For example, the use of an initial low temperature-low fluorine concentration reaction period followed by a higher temperature-high fluorine concentration reaction period results in

residual plutonium concentrations in the alumina bed of about 0.006 w/o for either reaction system; the re-use of an alumina bed for the fluorinations of several additions of U_3O_8 - PuO_2 -F.P. results in an almost linear increase in plutonium concentration on the alumina with each use up to a concentration of 0.2 to 0.3%, after which it remains at that level.

2. The results of the fluid-bed fluorination runs show that there does not appear to be any difference in the residual level of plutonium on the alumina whether mechanical mixtures of U_3O_8 and PuO_2 (separate components) or U_3O_8 - PuO_2 mixtures in which the PuO_2 was originally present as a solid solution with UO_2 are used. This fact is of interest to the feed material economy of the pilot plant.

The results also indicate that the lowest residual plutonium concentration obtainable on the alumina (0.004 w/o) is directly related to the quantity of plutonium fed to the alumina bed and is possibly independent of the presence of uranium or fission products when the feeding-fluorination period is conducted at temperatures no higher than 450° C.

The results obtained thus far are useful as an aid in selecting the process conditions which will give the lowest retention of plutonium on the alumina bed. The magnitude of the plutonium loss to be expected upon discarding the alumina to waste cannot yet be stated since this will depend upon a number of factors not yet determined, such as the number of times that the alumina bed can be re-used.

Future experimental work will be conducted in the present 1 1/2-in. diam. fluid-bed reactor and in a 2-in. diam. fluid-bed reactor now being tested. In addition to these two fluid-bed reactors, a 1 1/2-in. diam. horizontal tubular reactor will be employed for small-scale exploratory experiments.

One area of future investigation will be the use of fluorinating agents, such as HF , BrF_3 , and ClF_3 , to accomplish a prefluorination step. This will be followed by reaction with fluorine to produce the volatile hexafluorides. These experiments will be designed to determine whether there is any beneficial effect on plutonium retention by alumina of (1) altering the chemical form of the uranium, plutonium and fission products to fluorides, or (2) removal of uranium by fluorination with interhalogen gases prior to final fluorination with fluorine gas. Other investigations will include the study of static bed fluorinations, the use of higher reaction temperatures (650° C), and the fluorination of U_3O_8 - PuO_2 -F.P.- Al_2O_3 mixtures which will be fed into a reactor that does not contain an alumina bed.

Table II-6

SUMMARY OF DATA ON DECOMPOSITION OF GASEOUS PLUTONIUM HEXAFLUORIDE
BY ITS ALPHA RADIATION

Spherical Nickel Vessels: Volumes: 125-129 cc

Prefluorination Conditions: 1200 mm ClF_3 at 26°C for 1/2 hr, then 700 mm F_2 at 40°C for 1/2 hr,
and finally 620 mm F_2 at 100°C for 24 hr.

Temp ($^\circ\text{C}$)	PuF_6 Pressure (mm Hg)	Initial PuF_6 (mg)	Initial PuF_4 (mg)	Second Gas Component	Pressure of Second Gas (mm Hg)	No. of Experiments	Average Rate of PuF_6 Decomposi- tion (Percent per day) (No. of Days)	
							74.6 - 77	571
26	100	235	--	--	--	1	0.22 ^a	--
26	100	214-235	--	--	--	11	0.19 ± 0.03^b	--
26	100	223-237	12-350	--	--	25	0.14 ± 0.03	--
26	100	227-230	--	--	--	3	0.30 ± 0.03^c	--
26	100	232-233	42-46	--	--	2	0.16 ^c	--
82	100	230-233	--	--	--	4	0.64 ± 0.06	--
82	100	227-238	22-35	--	--	6	0.53 ± 0.12	--
26	100	216	--	Fluorine	138	1	0.082	--
26	100	233	--	Fluorine	395	1	0.13	--
26	100	215	--	Fluorine	3610	1	0.054	--
26	100	220	--	Oxygen	148	1	0.099	--
26	100	227	--	Oxygen	430	1	0.095	--
26	100	220	--	Oxygen	2610	1	0.11	--
26	100	218	--	Nitrogen	88	1	0.45	--
26	100	222	--	Nitrogen	119	1	0.47	--
26	100	221	--	Nitrogen	382	1	0.55	--
26	100	218	--	Nitrogen	1080	1	0.62^d	--
26	100	220	--	Nitrogen	2670	1	0.71^d	--
26	100	234	--	--	--	1	--	0.044
26	100	231-235	3.4,7.6	--	--	2	--	0.091
26	75	172	--	--	--	1	--	0.095
26	75	173	4.8	--	--	1	--	0.090
26	50	115-118	--	--	--	7	--	0.067 ± 0.008

^a This sphere was not prefluorinated.

^b All uncertainties listed are standard deviations.

^c These spheres were packed with nickel wool to increase the surface-to-volume ratio tenfold.

^d An infrared scan of the product gases after removal of PuF_6 showed NF_3 to be present.

2. Radiation Chemistry of Plutonium Hexafluoride

a. Alpha Decomposition of PuF₆

A study of the factors influencing the rate of alpha decomposition of PuF₆ has been continued to provide information useful to the fluid-bed fluoride volatility processes (see ANL-6766, p. 89). The conditions used in the experiments and the results obtained are given in Table II-6. The effects of the following factors on the decomposition of PuF₆ were examined: (1) length of storage time and initial PuF₆ pressure, (2) the presence of PuF₄ (from previous alpha decomposition runs), (3) storage temperature, (4) the presence of gaseous additives, such as fluorine, oxygen, and nitrogen, (5) surface-to-volume ratio, (6) pretreatment of storage spheres, and (7) storage container volume.

The effects of these various factors on the decomposition of PuF₆ can be assessed by comparing the results obtained in the various experiments with the results obtained in experiments in which the average PuF₆ decomposition rate was determined for samples of 100 mm Hg of pure PuF₆ stored in prefluorinated nickel spheres (127 ± 2 cc) at 26 ± 2° C for 75 days. Under these conditions, the average decomposition rate was 0.19 ± 0.03% per day.

Storage time and initial PuF₆ pressure. The average rate of decomposition of PuF₆ was found to decrease with time, as expected. For initial samples of 100 mm, 75 mm, and 50 mm of pure PuF₆ which were stored in prefluorinated test spheres (127 ± 2 cc) at 26 ± 2° C for 571 days, values of 0.044, 0.095, and 0.067% decomposition per day, respectively, were obtained. The value for the 100 mm sample of PuF₆ is inexplicably low when compared with the values for 75 mm and 50 mm samples of PuF₆.

Presence of PuF₄. When PuF₄ was initially present in the sphere, the decomposition rate of PuF₆ was found to decrease but was independent of the amount of PuF₄ initially present. In prefluorinated test spheres (127 ± 2 cc) that initially contained 100 mm Hg of PuF₆ and PuF₄ (varying from 12 to 350 mg) and were stored at 26 ± 2° C for about 75 days, the average decomposition rate was 0.14 ± 0.03% per day.

Storage temperature. The decomposition rate of PuF₆ was increased when the decomposition temperature was increased (from 26 ± 2° C to 82° C) in tests in which no PuF₄ was initially present. This leads to the belief that some thermal decomposition of PuF₆ takes place at the higher temperature, since purely radiation-induced decomposition should be independent of temperature. A rate of PuF₆ decomposition of 0.64 ± 0.06% per day was obtained for prefluorinated spheres (127 ± 2 cc) that contained 100 mm of pure PuF₆ and were held at 82 ± 2° C for 77 days. For spheres under similar conditions, but which contained 100 mm of PuF₆ and 22 to 35 mg of PuF₄ initially, the PuF₆ decomposition rate was less (0.53 ± 0.12% per day) than for spheres containing pure PuF₆.

Presence of fluorine, oxygen, and nitrogen. In these experiments, prefluorinated spheres (127 ± 2 cc) were filled with 100 mm Hg of PuF_6 and one of the gaseous additives (fluorine, oxygen, or nitrogen) and held at $26 \pm 2^\circ\text{C}$ for 75 days.

The presence of fluorine and oxygen decreased the decomposition rate. The decrease in decomposition rate was found to be independent of the pressure of the second gaseous component in the ranges studied. In runs with fluorine present to the extent of 138 mm, 395 mm, and 3610 mm, PuF_6 decomposition rates of 0.082, 0.13, and 0.054% per day, respectively, were obtained. When oxygen pressures were 148 mm, 430 mm, and 2610 mm, PuF_6 decomposed at rates of 0.099, 0.095, and 0.11% per day, respectively.

The presence of nitrogen was found to increase greatly the extent and the rate of PuF_6 decomposition. The high PuF_6 decomposition rates found in PuF_6 -nitrogen mixtures were due to a slow reaction between nitrogen and PuF_6 (or nitrogen and the fluorine formed) which produces NF_3 and PuF_4 . The amount of PuF_6 decomposed (0.45, 0.47, 0.55, 0.62, and 0.71% per day) increased with increasing nitrogen pressure (88, 119, 382, 1080, and 2670 mm).

Surface-to-volume ratio. Nickel spheres were packed with nickel wool to increase the surface-to-volume ratio tenfold, and were then prefluorinated. Experiments were carried out with spheres which contained either pure PuF_6 (100 mmHg) or PuF_6 (100 mm Hg) and some PuF_4 (from a previous alpha decomposition of PuF_6). The spheres were held at $26 \pm 2^\circ\text{C}$ for about 75 days. The decomposition rate was found to be significantly higher when the decomposition occurred in spheres that contained nickel wool and pure PuF_6 ($0.30 \pm 0.03\%$ per day) than in spheres that did not contain nickel wool. However, the rate was less (0.16% per day) in spheres that were packed with nickel wool and contained PuF_4 initially present than in spheres that contained nickel wool and pure PuF_6 .

Prefluorination of nickel spheres. The prefluorination procedure is performed by treating the spheres with 1200 mm of ClF_3 at 26°C for 1/2 hr, then with 700 mm of fluorine at 40°C for 1/2 hr, and finally with 620 mm of fluorine at 100°C for 24 hr. The results of a single experiment carried out in a nonprefluorinated nickel sphere (127 ± 2 cc) that contained 100 mm of pure PuF_6 and was held at $26 \pm 2^\circ\text{C}$ for 75 days indicated an average PuF_6 decomposition rate of 0.22% per day. This rate was higher than the rate (0.19% per day) obtained when prefluorinated spheres were used, but was lower than the rate (0.30% per day) obtained in spheres which were packed with nickel wool and prefluorinated.

Storage volume. An increase in the volume of the storage sphere resulted in a decrease in the decomposition rate. The results of a single experiment with a prefluorinated, 5.96-liter nickel sphere that contained 100 mm of pure PuF_6 and was held at $26 \pm 2^\circ\text{C}$ for 75 days indicated

an average decomposition rate of 0.11% per day.

b. Gamma Radiation Decomposition of PuF_6

The decomposition of plutonium hexafluoride is being studied to gain a broader understanding of the factors that affect the decomposition of this compound. The kinetics and mechanism of the thermal decomposition of PuF_6 have been investigated earlier (see ANL-6766, p. 85). The present study concerns the decomposition of PuF_6 by gamma radiation. In the course of the study, the effect of the addition of such gases as helium and krypton was also investigated.

In the study of the decomposition of plutonium hexafluoride by gamma radiation, gaseous plutonium hexafluoride is irradiated by fission product gamma radiation and the loss of plutonium hexafluoride is determined. The products of the decomposition are elemental fluorine and plutonium tetrafluoride. Previous results have indicated that the G^* value for the decomposition of pure plutonium hexafluoride is 7.5. Addition of one atmosphere of helium to plutonium hexafluoride at approximately 80 mm Hg pressures results in a G value for the decomposition which is not significantly different from that obtained with pure plutonium hexafluoride. When two atmospheres of helium are added to plutonium hexafluoride at about 80 mm Hg pressure, a significantly lower G value (5.8) is obtained.

In recent experiments, the effect of added krypton on the G value for the decomposition of plutonium hexafluoride has been investigated. Data obtained at an exposure dose of 1×10^8 rads and at various krypton concentrations are shown in Figure II-13. The G values, which were calculated on the basis of the energy absorbed only by the plutonium hexafluoride, permit direct comparison with the data given above. The marked enhancement of the G values for the decomposition at an exposure dose of 1×10^8 rads when the electron fractions of krypton were about 0.7 was not observed when similar experiments were carried out at an exposure dose of 2×10^8 rads. In the latter case, the values of G decreased continuously as the electron fraction of krypton, and hence, the concentration of krypton was increased.

It is believed that several competitive processes cause the marked increase in G values at an electron fraction of krypton of about 0.7. The initial drop in G values at lower electron fractions of krypton may be due to deactivation of excited or ionized plutonium hexafluoride molecules by krypton. As the concentration of krypton, and hence the energy absorbed in krypton increases, enhanced decomposition of plutonium hexafluoride by activated krypton may be responsible for the sharp rise in the G values. It should be mentioned that the formation of krypton fluorides would also result in an enhanced G value for the decomposition; however, no evidence to

* Molecules decomposed per 100 ev of absorbed radiation.

Figure II-13

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE BY GAMMA RADIATION IN MIXTURES WITH KRYPTON

Exposure dose: 1×10^8 rads ($\sim 15 \times 10^{20}$ ev absorbed in PuF_6). G calculated only from energy absorbed in PuF_6 . G value is number of molecules of PuF_6 decomposed per 100 ev of absorbed radiation.

substantiate this possibility was obtained in these experiments.

At still larger concentrations of krypton, the deactivation of highly excited plutonium hexafluoride, or the enhancement of the back reaction, that is, the reaction of plutonium tetrafluoride and fluorine to form plutonium hexafluoride, may be responsible for the decrease in the G value for the decomposition. Although evidence for the mechanisms suggested earlier is lacking, data to corroborate the effect of the back reaction have been obtained from experiments in which mixtures of plutonium tetrafluoride and elemental fluorine were irradiated by gamma radiation. In these experiments, significant quantities of plutonium hexafluoride were produced, and the pressures of plutonium hexafluoride obtained were in excess of those which would be predicted from the usual thermodynamic equilibrium considerations alone. Although several reactions can be proposed and in part supported by experiments, no unequivocal mechanism has been developed which would allow the correlation of all the experimental data, and particularly the unusual differences that exist between the effect of krypton at 1×10^8 rads and at 2×10^8 rads.

The work on gamma radiation decomposition of PuF_6 has been completed except for final correlating and reporting of the data.

3. Absorption Spectrum of Gaseous Plutonium Hexafluoride

As a supplement to the study of the radiation chemistry of plutonium hexafluoride and in order to develop methods of quantitative analysis for plutonium hexafluoride in mixtures of uranium hexafluoride and plutonium

Figure II-14

ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE

hexafluoride, the absorption spectrum of gaseous plutonium hexafluoride (see ANL-6766, p. 92) has been determined in the near infrared, the visible and the ultraviolet region of the spectrum. The absorption spectrum of gaseous plutonium hexafluoride was determined on a Cary Model 14 recording spectrophotometer at ambient laboratory temperatures in cells using quartz windows. The results are shown in Figure II-14, where the molar absorptivity index is plotted against the energy in wave numbers. The two major bands in the near infrared region of the spectrum exhibit discernible fine structure and the peak separations can be correlated with the known vibrational spectrum of the plutonium hexafluoride molecule. Further, some of the remaining bands have been correlated with the absorption spectra observed for the isoelectronic series U(IV), Np(V) and Pu(VI).

In order to utilize these data for the analysis of plutonium hexafluoride in mixtures of uranium hexafluoride and plutonium hexafluoride, Beer's law plots were made at two wave lengths (3157 Å and 10075 Å) and proved to be straight lines. Determination of molar extinction coefficients of mixtures of UF_6 and PuF_6 were made and agreed adequately with calculated data determined from Beer's law. However, in order to use spectral properties for precise analysis of mixtures of UF_6 and PuF_6 , additional attention to window materials and accurate determination of calibration curves are required.

No further work is planned in the development of this method for the analysis of PuF_6 in mixtures of UF_6 and PuF_6 . The results of this study have been accepted for publication in the literature.

4. Phase Studies

Preparations are being made for experimental studies of the vapor-liquid and liquid-solid phase equilibria in the system PuF_6 - UF_6 . The results of these studies will be useful in the choice of conditions for fluoride volatility processes and will also provide basic data of importance to the understanding of the chemistry of this system.

The phase studies will be carried out in the presence of solid PuF_4 because it is continuously produced from the alpha radiation-induced decomposition of PuF_6 . The solubility of PuF_4 in PuF_6 and in UF_6 , and in mixtures of UF_6 and PuF_6 will be determined.

The study of the liquid-vapor equilibria of the system PuF_6 - UF_6 will be done in an equilibrium still of the type in which vapor is recirculated through the liquid phase. A drawing of the apparatus is given in Figure II-15. The still and vapor loop, which will be inside a large, isothermal box, will be maintained at a selected temperature between 70 and 90°C. Phase composition and pressure data will be obtained as a function of temperature. These data will be especially useful in the study of the fractional distillation of PuF_6 - UF_6 mixtures.

Figure II-15

VAPOR-LIQUID EQUILIBRIUM APPARATUS

Apparatus is also being constructed for obtaining the temperature-composition diagram of solid-liquid equilibria in the system $\text{PuF}_6\text{-UF}_6$. The techniques of thermal analysis and differential thermal analysis will be employed in this work.

5. Program of Research on Neptunium Hexafluoride

A program of research on the chemistry of neptunium hexafluoride is being started. A long-lived neptunium isotope (Np^{237}) is formed as a minor constituent in irradiated reactor fuel and, owing to the physical properties of neptunium hexafluoride, contamination of uranium or plutonium in the fluid-bed fluoride volatility process by small quantities of neptunium hexafluoride is expected. Little or no information on the chemical properties of neptunium hexafluoride is available. The program as currently planned is designed to examine the rates of formation of neptunium hexafluoride from the tetrafluoride and to study the equilibrium in the system neptunium hexafluoride-neptunium tetrafluoride-fluorine. The absorption spectrum of neptunium hexafluoride will be determined, and its use as a means of analysis for neptunium hexafluoride will be examined.

III. HIGH TEMPERATURE FUELS AND MATERIALS DEVELOPMENT

A program directed toward the development of high temperature nuclear reactor fuels and materials is under way. The general area of study is concerned with the chemical stability and chemical reactions of potential fuels (such as oxides, sulfides, and phosphides, of uranium and some of their solid solution alloys) with their possible reactor environments (such as hydrogen and possible contaminating gases) and supporting refractory components (such as tungsten, rhenium, molybdenum, tantalum and certain of their alloys).

The objective is to build up a reservoir of basic data from which needed information for evaluation may be drawn. The approach is to study the relevant chemical systems in a quantitative manner so as to obtain thermodynamic evaluations. Each selected fuel-refractory metal-gas system is to be studied in an integrated way, using several primary methods of high temperature investigations that are mutually supporting.

Program planning was initiated in March 1963, and the main efforts to date have been devoted to the planning, acquisition, installation, and adaptation of equipment for the projected measurements. Studies of the vapor-condensed state equilibria in the uranium-uranium dioxide system are in progress.

A. Estimation of the Nature of the High Temperature Phase Relations in the Uranium-Uranium Dioxide-Hydrogen System

From the data in the literature on uranium-uranium dioxide studies, the schematic representations in Figs. III-1 and III-2 for two isothermal cross-sections are considered probable in form and useful for discussion and research planning purposes. The pressure-composition phase diagram at 1627° C, shown in Fig. III-1, is based primarily on a similar figure given by Ackermann and Thorn,¹ but Fig. III-1 also incorporates the concept of the probable existence of a substoichiometric range^{2,3} for uranium dioxide. Except for the points, a, d, and g, none of the phase boundaries have been established. The pressure-composition phase diagram at 2400° C, shown in Fig. III-2, is speculative and is based on extrapolation of literature data¹ and discussions with Ackermann and Thorn⁴, particularly on the congruency of

¹ Thermodynamics of Nuclear Materials, Proceedings of the Symposium on Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna, May 1962, pp. 445-464.

² Rand, M. H. and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963, p. 29.

³ Aitken, E. A., Brassfield, H. C. and McGurty, J. A., Transactions of the American Nuclear Society, June 1963, p. 153.

⁴ Thorn, R. J. and Ackermann, R. J., Argonne National Laboratory, private communications, November 1963.

Figure III-1

SCHEMATIC DIAGRAM FOR THE URANIUM-URANIUM
DIOXIDE SYSTEM AT 1627° C

(Only the points a, d and g can be considered reliable.)
(Uranium dioxide is assumed to vary in stoichiometry by $\pm x$.)

vaporization of uranium dioxide. The work of Ackermann, Gilles, and Thorn⁵ established that the vaporization of uranium dioxide at temperatures to 2200° C from effusion cells to vacuum yielded stoichiometric uranium dioxide residues within the cell. A few recent unpublished measurements⁴ show that this behavior prevails to 2400° C. Thus, the positioning of the points, g, in the two figures is considered reliable with regard to composition, although conflicting information² exists. The points a and d at 2400° C are reasonable estimates. The existence of hyperstoichiometric uranium dioxide is well established,⁶ but no reliable information for the phase boundary g-f exists for the temperature range under consideration (1627 - 2400° C).

It is apparent from Figs. III-1 and -2 that adequate reducing conditions would lead to the reduction of uranium dioxide to form liquid uranium-oxygen

⁵ Ackermann, R. J., Gilles, P. W. and Thorn, R. J., J. Chem. Phys. 25, 1089 (1956).

⁶ Rand, M. H. and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963, p. 26.

Figure III-2

SCHEMATIC SPECULATIVE DIAGRAM FOR THE URANIUM-URANIUM DIOXIDE SYSTEM AT 2400°C

(Points a, d and g are based on reasonable extrapolations.)
 (Uranium dioxide is assumed to vary in stoichiometry by $\pm x$.)

solutions. Because of the lack of thermodynamic data and knowledge of the true phase boundaries, the hydrogen pressures required to reach the c-d-e equilibria cannot be accurately calculated. However, if one considers the nonequilibrium situation in which hydrogen is passed over uranium dioxide and the reaction product, water vapor, is swept away, it is apparent that two competing processes would arise. (1) A reduction of the stoichiometric uranium dioxide solid would necessarily be initiated by the hydrogen and the composition of the solid would tend to change in the direction g-j. (2) Normal volatilization of the substoichiometric solid of composition, j, so produced, would tend to change the composition of the solid in the opposite direction j-g. If the first of these two processes is dominating, the reduction of the uranium dioxide along the path g-j-e-d-c could take place and lead to the formation of the liquid uranium-oxygen phase. Experiments by Aitken, Brassfield and McGurty³, in which hydrogen at one atmosphere was flowed slowly over uranium dioxide, demonstrate that reduction as far as an overall oxygen-to-uranium ratio of 1.88 was achieved at 2400°C. Their data suggest that this value is a limiting composition for the conditions of the experiment. They also performed one experiment in which a mixture of uranium and uranium dioxide having an oxygen-to-uranium ratio of 1.75

was made into a pellet. The pellet was subjected to prolonged heat treatment in the same type of flowing hydrogen atmosphere, but at 2600°C ; and the final oxygen-to-uranium ratio of this pellet was 1.89. Metallographic examinations of all the specimens (cooled from 1500°C in helium to prevent possible hydriding of any free uranium) showed the presence of both uranium metal and uranium dioxide. It is to be assumed that the uranium precipitated out from a substoichiometric solid (such as along e-j-g of Fig. III-2), yielding essentially stoichiometric² uranium dioxide.

The nature of the diagrams in Figs. III-1 and -2 indicates that any reduction of stoichiometric uranium dioxide leads to higher vapor pressures and greater volatility losses. The use of this material at high temperatures under reducing conditions would require cladding by some refractory material to inhibit volatility losses. Studies of interdiffusion between the fuels of interest and the refractory metals are a part of the program and will have importance with regard to experimentation containers and cladding problems.

B. Experimental Approaches

1. Effusion Vapor Pressure Studies

Measurements of the rates of vaporization for substoichiometric uranium dioxide-liquid uranium compositions (c-d-e plateau) will be carried out as a function of temperature in the range 1600 to 2200°C . A Knudsen effusion apparatus will be used in the studies. Similar measurements are to be carried out for a series of compositions along the e-j-g substoichiometric boundary and also along the a-b''-b-c and a-c boundaries of Figs. III-1 and -2, respectively, if a suitable container technique can be devised.

Preparation of tungsten effusion cells is underway. Fabrication of uranium dioxide cups to contain the liquid uranium (to establish c-d-e within the cell) is in progress.

The above described studies are being done in collaboration with R. J. Ackermann and R. J. Thorn of the Chemistry Division using their equipment. Design work is in progress for a suitable experimental apparatus for the Chemical Engineering Division so that additional effusion studies can be carried out.

2. Mass Spectrometric Effusion Studies

Mass spectrometric effusion studies paralleling the above described effusion measurements will be made to determine the gas phase boundaries with specific regard to the relative concentrations of the vaporizing gaseous species. In this general method, a Knudsen effusion cell containing the solid under investigation is heated to a high temperature and the effusing gas beam is then ionized by electron bombardment. The relative intensities of the

Figure III-3

BENDIX TIME-OF-FLIGHT MASS SPECTROMETER AND ACCESSORIES FOR HIGH TEMPERATURE KNUDSEN EFFUSION MEASUREMENTS

The effusion stack assembly is shown just as its top is being inserted within the mass spectrometer's port. The effusion cell, which is used to beam the vaporizing species to the ionizing zone of the mass spectrometer, is at the top of the stack surrounded by cylindrical tantalum radiation shields. Radiation shielding disks are visible at both the top and bottom of the effusion cell. Four tungsten posts, two of which are visible, support the top radiation shields. A tungsten filament (not visible) network is used to heat the cell by electron bombardment. The various other components are electrical leads and insulating spacers. Cell temperatures of 2900°C have been achieved.

various species in the gas are measured by the mass spectrometer (Fig. III-3). A second type of cell arrangement is also to be used in these studies. It will have a provision for introduction of gases directly to the cell through a small tungsten capillary tube. Thus it should be possible to introduce either dry hydrogen or hydrogen-water vapor mixtures to the cell to influence the equilibria within. Initially, studies will be made of the isothermal reductions of uranium dioxide along the g-j-e boundary. The extent of reduction will be

controlled by employing fixed gaseous ratios. The equilibrium condition will be identified by the attainment of constant concentrations of the various uranium-oxygen species. The composition of the residual material will be determined by chemical analysis. Thermodynamic evaluations should be possible from the data on the composition of the gas phase. A search for any new uranium-bearing species in the presence of the hydrogen-water vapor mixtures will be made. The existence of species of the type $U_aO_\beta H_\gamma$ (a , β and γ are undetermined integers) is considered possible.

Construction of the two Knudsen cell assemblies is nearly complete. The mass spectrometer (Bendix-Time-of-Flight) has been installed and is functioning satisfactorily.

3. Transpiration Studies of Vaporization

Extension of the vapor pressure measurements to higher temperatures than those possible in the effusion measurements is to be carried out by use of the transpiration method. In this method, an inert carrier gas is slowly over preparations having uranium-oxygen compositions of interest. The transported material is collected through a small sample tube and analyzed. The data can yield equilibrium partial pressures of the various species when thermodynamic data for the species in the gas phase are adequate.

In particular, it is planned to study the volatility transport from uranium dioxide with hydrogen and hydrogen-water mixtures as reactant carrier gases. Alexander and Levy,⁷ in a single transpiration measurement at 1510°C, observed a decidedly enhanced volatility from uranium dioxide when the carrier gas was hydrogen at one atmosphere of pressure. A reduction of uranium dioxide by hydrogen along the path g-j-e would lead to such a result.

The principal equipment for the work should be on hand shortly. Container and sample tubes will be fabricated from tungsten metal. Measurements at temperatures as high as 2800°C are considered feasible.

4. Phase Diagram Studies

Our knowledge of the uranium-uranium dioxide system is to be augmented by studies in the condensed state by the conventional thermal analysis and metallographic techniques. It is of particular interest to know what happens to the liquidus temperature of the uranium dioxide phase as that phase exceeds the saturation limit with respect to uranium. Some lowering of the liquidus temperature leading to a second liquid of a composition in the d-e range is considered probable. It is even conceivable that

⁷ Alexander, C. A. and Levy, A., BMI-1546, p. L-26.

the oxygen-rich liquid phase region could penetrate through the c-d-e horizontal boundary presented in Fig.III-2. A search for a three-phase monotectic arrest could clarify this assumption. Duncan and Ferrari⁸, however, report an elevation of the liquidus temperature for the substoichiometric uranium dioxide. Further study is needed to clarify the behavior of the liquidus.

Preceding discussions have purposely neglected the role that a third component (refractory metal container) might play in the experiments. However, uranium liquid is known to dissolve appreciable quantities of the most promising metals (those having the highest melting points and the lowest solubility for uranium), such as tungsten and tantalum. It is evident then that studies involving the presence of the liquid uranium phase must involve also the refractory metal container as a component. It is also evident that, if the assumption of the paragraph immediately above is correct, the additional refractory metal will interact with the uranium-uranium dioxide system whenever a liquid uranium phase is present and hence the ternary system requires consideration. Tungsten metal is to be used as the container material in most of the initial experimentation.

Prior to the initiation of the work with uranium dioxide, some exploratory experimentation was carried out with uranium monosulfide. Metal-uranium monosulfide mixtures were melted together by use of arc melting equipment. The metals used were tantalum, niobium, vanadium, tungsten, molybdenum, chromium, and rhenium. The low melting metals, chromium, vanadium, and niobium, were included because of generic relations to other metals in their respective columns in the periodic chart. Metallographic examinations of each of the quenched uranium monosulfide-metal melts revealed that two immiscible liquids (a metal-rich liquid and a uranium sulfide-rich liquid) had formed at the temperature of the arc melting. On freezing, each of the systems formed principally a uranium monosulfide phase and a metal phase. One or more additional phases were also formed. Results of X-ray diffraction examinations indicated that uranium sesquisulfide was the principal additional phase. The formation of uranium sesquisulfide is not expressible in terms of a simple binary phase diagram between the refractory metal and uranium monosulfide. A third component would be required to express the general phase relations. Thus, the interaction of uranium monosulfide with the refractory metals under consideration appears, from the exploratory arc melting experiments, to require studies in selected regions of the ternary systems, uranium-sulfur-refractory metal. Quantitative experimentation for those systems involving the most refractory metals is projected for some future date, dependent upon the progress of the uranium dioxide work described above.

High temperature vacuum furnace equipment is being assembled so that well-defined conditions of heat treatment can be obtained for the general

⁸ Duncan, R. N. and Ferrari, H. M., Transactions of the American Nuclear Society, Hinsdale, Illinois, June 1963, p. 154.

phase diagram studies. Equipment for other study techniques, such as differential thermal analysis, will be set up as time permits.

5. Interdiffusion Studies

Interdiffusion studies of the refractory metals and the refractory fuel materials are planned. The rate of diffusion of a high temperature fuel through potential refractory metal claddings is of obvious importance. Moreover, effective experimentation in the several studies discussed above requires knowledge of diffusion limitations, since the same refractory metals are being considered for use as container materials.

A preliminary experiment is being planned in which uranium monosulfide will be sealed (by electron beam welding) within a tungsten crucible, which will be held for an hour at a temperature slightly above the melting point of uranium monosulfide. Weight losses, if any, will be measured. Metallographic analysis will be carried out to assess the relative importance of attack at tungsten grain boundaries versus bulk diffusion. Studies of single crystals of tungsten, after controlled heat treatments in molten uranium monosulfide, are projected. Electron probe microanalyses will be carried out to determine the concentration gradients if they are in the measurable range.

A vacuum induction furnace is being assembled for the general interdiffusion studies.

IV. CALORIMETRY

The calorimetry program is directed toward the determination of thermodynamic data for compounds of interest in high temperature chemistry. During the past year the main effort has been devoted to the determination of room temperature enthalpies of formation by means of fluorine bomb calorimetry. Effort has also been made to establish means for making high temperature enthalpy measurements. Toward this end, two calorimeters have been designed: one operable to 1500°C, and the other operable to 2500°C. Subassemblies for the 1500°C calorimeter have been constructed and are being tested.

A. Fluorine Bomb Calorimetry

The method of fluorine bomb calorimetry continues to be productive.¹ However, as the work has proceeded in this field and new, improved techniques have been developed, it has been necessary to reassess earlier work whenever new developments have indicated that uncertainties in earlier work might be appreciably reduced by the application of the improved techniques. During the past year, several instances of this nature have been encountered.

In the initial studies of the heats of formation of magnesium difluoride and aluminum trifluoride (see ANL-6766, p. 95), large uncertainties were present even though the studies were carried out by the same technique that was used in the satisfactory studies of cadmium difluoride and zinc difluoride. For all of these combustions, the samples were supported on dishes made of compressed fluorides (in each case, the fluoride of the metal studied). For the combustions of magnesium and aluminum, the fluoride support material contained excessive amounts of oxides, part of which reacted with the fluorine. An uncomfortably large thermal correction was required. Moreover, the combustions were only 85 to 95% complete, and required a correction for unburned sample. During the past year, techniques were developed for exposure

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- ¹ a. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry. V. The Heats of Formation of Silicon Tetrafluoride and Silica, *J. Phys. Chem.*, 67, 815 (1963).
- b. J. L. Settle, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry. VI. The Enthalpy of Formation of Uranium Hexafluoride, *J. Phys. Chem.*, 67, 1892 (1963).
- c. E. Rudzitis, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry. VII. The Heat of Formation of Cadmium Difluoride, *J. Phys. Chem.*, 67, 2388 (1963).
- d. E. Rudzitis, R. Terry, H. M. Feder, and W. N. Hubbard, Fluorine Bomb Calorimetry. VIII. The Heat of Formation of Zinc Difluoride, Accepted for publication in *J. Phys. Chem.*

Figure IV-1

COMBUSTION BOMB WITH SAMPLE ARRANGEMENT FOR COMBUSTIONS OF MAGNESIUM AND YTTRIUM

of the fluoride support materials to anhydrous HF at pressures up to 200 atmospheres and temperatures up to 200° C prior to fabrication of the supports, in order to minimize the oxide content. An improved sample arrangement was developed in which the sample is suspended in a fluoride-lined bomb during part of its combustion. Both the bomb body and the bomb cap are lined with a layer, approximately 1/4 in. thick, of the fluoride of the metal studied, as shown in Figure IV-1. The sample falls to the fluoride-covered lining of the bomb only for the last phases of combustion. This technique was used for a second series of measurements on magnesium difluoride. Combustions with the new arrangement were 99.6 to 99.9% complete. The precision of the results appears improved, although final calculations have not been made. The new sample arrangement is being used in a new study of the enthalpy of formation of yttrium trifluoride and will also be used for a second series of aluminum combustions and for combustions of several of the rare earths.

Another example of improvement in techniques was in the study of the enthalpy of formation of zirconium diboride. For these studies, the two-compartment combustion vessel² was used (Fig. IV-2). The zirconium sample support dish (not shown) rests inside the retaining ring. A known amount of sulfur is spread in a thin layer on the central portion of the dish and is covered

² R. L. Nuttall, S. S. Wise, and W. N. Hubbard, Combustion Bomb Reaction Vessel for Spontaneously Reacting Materials, Rev. Sci. Instr. 32, 1402 (1961).

with diboride sample. The sulfur provides positive spontaneous ignition when fluorine is introduced and promotes combustion. The electrodes of the bomb are not used in this work.

Figure IV-2

COMBUSTION BOMB AND FLUORINE CHAMBER FOR COMBUSTIONS
OF THE DIBORIDES OF ZIRCONIUM, HAFNIUM, AND NIOBIUM

There were two problems associated with the first series of measurements. When the two-compartment vessel is used, the first exposure of fluorine to the interior of the bomb occurs at the start of the main reaction period when ignition is desired. A significant amount of reaction between fluorine and another material (presumably moisture absorbed on the walls) occurs, necessitating a thermal correction. For the conditions of the experiments, the magnitude of this correction (determined by blank experiments) was undesirably large. The second problem pertained to fluorine attack of the zirconium dish which was the sample support. Corrections for this reaction could not be made reliably. Improvements in technique subsequently developed were pre-exposure of the bomb to boron trifluoride gas, which greatly lowered the necessary blank correction, and the use of a heavier zirconium support dish. In the second series of calorimetric combustions, carried out during the past year, the blank correction was considerably smaller than in the first series, and the

fluorine attack on the zirconium dish was satisfactorily small because the dish remained cooler. An additional consequence of the improved techniques was that the precision of the results was also considerably improved. The results of the second series of combustions, which was carried out on a sample of composition $\text{ZrB}_{2.01}$, are:

$$\Delta \text{Ec}_{298}^\circ = -922.0 \pm 0.3 \text{ kcal/mole}$$

For calculating the enthalpy of formation of ZrB_2 , values previously obtained in this laboratory for ZrF_4 ³ and BF_3 ⁴ were used:

$$\Delta \text{Hf}_{298}^\circ = -76 \pm 5.8 \text{ kcal/mole}$$

The large uncertainty in the enthalpy of formation value is primarily attributable to the uncertainty in defining the stoichiometric ratio of boron to zirconium. Although the heat of combustion has been assigned to $\text{ZrB}_{2.01}$, an uncertainty of ± 0.02 is assigned to the stoichiometric ratio to reflect the accuracy of sample analysis. An error of 0.01 in the stoichiometric ratio would result in an error of 2.7 kcal/mole in the heat of formation. This problem is inherent in the study of compounds that exist over a range of composition if one or more of the constituent elements is not amenable to accurate (0.1% or better) analysis.

The improved techniques developed for zirconium diboride have also been used during the past year for determinations of the enthalpies of formation of the diborides of hafnium and niobium. The preliminary results of the study on hafnium diboride are:

$$\Delta \text{Ec}_{298}^\circ = -928.2 \pm 0.2 \text{ kcal/mole}$$

$$\Delta \text{Hf}_{298}^\circ = -76.6 \pm 5.8 \text{ kcal/mole}$$

The results of the study of niobium diboride have not as yet been calculated.

³ E. Greenberg, J. L. Settle, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry. I. The Heat of Formation of Zirconium Tetrafluoride, J. Phys. Chem., 65, 1168 (1961).

⁴ S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry. III. The Heat of Formation of Boron Trifluoride, J. Phys. Chem., 65, 2157 (1961).

A final example of the improvement in techniques is seen in the combustion experiments with tantalum in fluorine. The first series was repeated with modifications in techniques (improved sample geometry and improved combustion product recovery) that led to improved accuracy and precision. These techniques were also used in combustions of niobium and ruthenium. The sample arrangement for the study of these compounds is shown in Figure IV-3. The results of the three studies are:

$$\Delta \text{Ec}_{298}^\circ = -453.6 \pm 0.07 \text{ kcal/mole}$$

$$\Delta \text{Hf}_{298}^\circ = -455.1 \pm 0.3 \text{ kcal/mole}$$

$$\Delta \text{Ec}_{298}^\circ = -432.0 \pm 0.03 \text{ kcal/mole}$$

$$\Delta \text{Hf}_{298}^\circ = -433.5 \pm 0.2 \text{ kcal/mole}$$

$$\Delta \text{Ec}_{298}^\circ = -211.9 \pm 0.2 \text{ kcal/mole}$$

$$\Delta \text{Hf}_{298}^\circ = -213.4 \pm 0.4 \text{ kcal/mole}$$

Presently, the enthalpy of combustion of two forms (alpha and beta) of silicon carbide in fluorine is being determined in an attempt to obtain a better value for the enthalpy of formation of silicon carbide, for which literature values range over 8 kcal/mole.^{1a} The value of the latter thermodynamic quantity depends on values of the enthalpies of formation of silicon tetrafluoride and tetrafluoromethane. A value for the former^{1a} has been determined, and attempts are being made to obtain a better value for the latter by combustion of graphite or diamond in fluorine, since the best literature values for tetrafluoromethane range over 3 kcal/mole.

Exploratory work is also continuing on the development of techniques for the combustion of uranium compounds in fluorine. Considerable uncertainty exists in the thermochemistry of uranium compounds because of the difficulty of preparing adequately characterized samples for study and the difficulty of devising suitable combustion techniques since many of the uranium compounds react readily with fluorine and must be protected from fluorine until ignition is desired. Considerable effort has been spent by a subcontractor to prepare well-characterized samples of binary uranium compounds. An attempt will be made to carry out the combustion of samples in a flow calorimeter. The first compounds studied will probably be the sulfides and phosphides of uranium.

Figure IV-3

COMBUSTION BOMB WITH SAMPLE ARRANGEMENT FOR COMBUSTIONS OF TANTALUM, NIOBIUM AND RUTHENIUM

Calculation of the Enthalpy of Formation of Hydrogen Fluoride

An interesting result of previous work in fluorine bomb calorimetry was the calculation of a new value for the enthalpy of formation of hydrogen fluoride.⁵ In an earlier study, combustions of α -quartz in fluorine were carried out.^{1a} The α -quartz combustions led to a value for the enthalpy change in reaction 1:

$$\Delta H_1 = -168.26 \pm 0.28 \text{ kcal/mole} \quad (1)$$

The results of this study were combined with a study by Lenfesty, Farr, and Brosheer⁶ of the equilibrium between α -quartz, hydrogen fluoride, silicon tetrafluoride and water. The equilibrium experiments led to a value for the

⁵ H. M. Feder, J. L. Margrave, W. N. Hubbard, and S. S. Wise, The Heat of Formation of Hydrogen Fluoride, J. Phys. Chem., 67, 1148 (1963).

⁶ F. A. Lenfesty, T. D. Farr and J. C. Brosheer, Ind. Eng. Chem., 44, 1448 (1952).

the enthalpy change in reaction 2:

$$\Delta H_2 = -24.18 \pm 0.35 \text{ kcal/mole} \quad (2)$$

Addition of the two reactions and twice the enthalpy of formation of water, reaction 3:

gives the enthalpy change for the formation of four moles of hydrogen fluoride, reaction 4:

Thus, the standard enthalpy of formation of one mole of hydrogen fluoride gas is -64.92 kcal/mole . Because four moles of hydrogen fluoride are involved, the uncertainty per mole is small, -0.15 kcal . Previous to this work, the "selected" best value for ΔH_{298}° (HF, g) was -64.2 kcal/mole .⁷

B. High Temperature Enthalpy Calorimetry

Parts for a calorimetric system for measuring enthalpy increments up to 1500°C have been constructed. Various subassemblies have been assembled and are undergoing testing. This calorimeter is of the drop type and consists of a drop mechanism and drop tube which rests on a furnace where the sample is heated, a gate through which the heated sample is dropped, and a calorimeter where the heat evolved by the sample is measured.

The drop mechanism and drop tube have been assembled with the associated electronic circuitry. The sample hangs in the furnace suspended by a wire from a weight appropriately positioned in the drop tube. The weight in turn is suspended by a metal tape that is wound on the drum of an eddy current brake. When the weight is released, the sample falls to the calorimeter. As the sample approaches the calorimeter, the weight (which contains four permanent magnets) passes through a coil wound outside the drop tube, causing an electronic pulse that is amplified and used to actuate the magnet of the eddy current brake. The sample is decelerated and comes to rest in the calorimeter. It is possible to drop the sample at different rates by varying the trickle current through the eddy current brake. Dropping the sample at different rates will allow the heat lost during the drop to be determined by extrapolation to zero time. This subassembly has been tested, and the deceleration rate has

⁷ F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, Washington, D. C. (1952).

been studied as a function of electromagnetic current by photography using stroboscopic light.

The furnace has been assembled with its associated control circuitry. After repeated thermal cycling, it was found that the dust shield (ANL-6477, p. 165) had buckled and that some of the silver shields had melted where they contacted aluminum. Presumably, a low-melting alloy of silver and aluminum was formed. The furnace has been reassembled repeatedly since then to test the insulation efficiency of various powders in the dust shield, the behavior of various thermocouples, and the use of different heating cores. The heating core consists of the parts of the furnace inside the dust shield, comprising one or more units on which the resistance heating coils are wound. The different cores tried were a 3-unit molybdenum core and single-unit Alundum and Morganite cores with various heating coil windings.

It has been found that: (1) 1000 mesh silicon carbide has as good thermal properties for a dust shield filler as anything else tested and has the advantage of rapid degassing; (2) although sheathed thermocouples are more difficult to install, their use minimizes undesirable electrical pickup from the heater circuits; and (3) Morganite cores may be used. An alternative to the use of a dust shield is next to be tested. A spirally wound shield of approximately twenty laps (1/16 in. apart) of 0.003-in. molybdenum will be tried in place of the dust shield. This arrangement will have a minimum degassing time and hopefully will stand thermal cycling better.

The gate mechanism has been assembled with its vacuum system and has been tested while installed at the bottom of the furnace. It appears to function satisfactorily. When the gate is closed around the drop wire, it will hold a vacuum of 10^{-5} mm mercury pressure against the room atmosphere.

Two units, either of which may serve as the calorimeter proper, have been designed. The more versatile one is an adiabatic calorimeter capable of operation up to 400° . It has not as yet been completely assembled. The other one is a copper block calorimeter of the constant-temperature environment type which will operate only at approximately 25°C . It has been assembled and tested with its associated thermometry and heating circuitry. It is currently being calibrated by electrical heating. A diagram of the latter calorimeter is shown in Figure IV-4. This calorimeter comprises: (1) a copper block, the temperature rise of which is proportional to the heat evolved by the sample, (2) a constant-temperature jacket, through which water is pumped from a constant-temperature bath, (3) a central tube, through which a heated sample may be dropped into the block, and (4) two manually operated shutters that can be opened briefly for a sample drop. The upper shutter serves to transfer radiant energy from the furnace to the water bath. The lower shutter transfers radiant energy from the sample to the copper block.

Figure IV-4

COPPER BLOCK CALORIMETER

It is expected that these subassemblies of the 1500°C calorimetric system will be assembled and tested soon. Satisfactory tests will mean that calorimetric measurements can be started.

A drop calorimetric system for operation up to 2500°C has also been designed. For the furnace, electron bombardment heating will be used. The electron beam guns and their associated power supply and controls have been tested in a mock-up furnace, and functioned satisfactorily. Drawings for the entire system are complete. The support stand, furnace, and its shielding are under construction, and fabrication is nearly complete. The copper block calorimeter discussed above was designed for the initial measurements with either system and thus may be used with the 2500°C furnace.

V. REACTOR SAFETY

The program on reactor safety is comprised of two major areas of research: (1) the study of metal-water reactions and (2) the study of the oxidation and ignition processes of substances used in reactor technology.

A. Metal-Water Reactions

Interest in metal-water reactions stems from the large liberation of heat that could conceivably result from an accident in a water-cooled reactor. A coolant failure or a severe nuclear excursion could cause melting and rapid dispersion of the reactor core metals into the cooling water. This might lead to a highly exothermic chemical reaction between the metals and the cooling water. The energy released by such a reaction could exceed that released by the fission process during a nuclear excursion.

The current program for the study of metal-water reactions and past achievements in the program can be divided into four categories. The first of these involves the experimental determination of the isothermal rate law and rate constants. These are needed in order to develop mathematical expressions of the reaction rate as a function of time and temperature for use in accident calculations. Isothermal studies also locate characteristic temperatures for each reaction at which the nature of the reaction mechanism or products changes sharply. The second category covers nonisothermal studies of the reactions of small metal particles in order to simulate accidental situations under idealized conditions. These experiments have helped to evaluate the role of gas-phase diffusion and heat transfer in the overall process. The third category includes the in-pile studies in TREAT in which there is a more direct simulation of reactor excursion accidents and in which the nature and degree of fragmentation of representative fuel element specimens is determined. In the fourth category are included calculational studies and accident analyses in which the experimental results from different methods are compared and methods of accident analysis devised.

1. Isothermal Reaction Rate Studies

It has been necessary to develop a series of unique experimental methods in order to study the steam reaction of metals having widely differing properties. The methods and the work accomplished by means of each method are listed in Table V-1.

In the pressure pulse method, molten metal contained in a crucible in an evacuated reaction cell is brought to the desired temperature by induction heating. Electronically controlled valves are operated in proper sequence to contact the molten metal with one-atm steam for a specified period of time. Extent of metal-water reaction is determined by analysis of the exit gas for hydrogen. The volumetric method, the levitation-melting method and the high

Table V-1

STATUS OF ISOTHERMAL REACTION RATE STUDIES

<u>Metal</u>	<u>Pressure Pulse Method</u>	<u>Volumetric Method</u>	<u>Levitation- Melting Method</u>	<u>High Pressure Furnace Method</u>	<u>Other Institution^a</u>
Zirconium	-	-	-	-	Available 1000-1850°C
Aluminum	Completed 800-1200°C	-	Completed 1200-1800°C	Apparatus under construction for studies up to 1000 psi and 1900°C	-
Aluminum, 17 w/o Uranium, 2 w/o Nickel ^b	-	-	In progress 1200-1800°C	-	-
Stainless Steel	-	Results unsatisfactory	-	-	-
Uranium	-	Completed 400-1600°C	-	-	-
Molybdenum	-	In progress 1100-1700°C	-	-	-

^a Isothermal data available from studies at Battelle Memorial Institute and Westinghouse Corporation. These results were previously shown to be consistent with our results by the condenser discharge method and further isothermal studies were considered unnecessary.

^b SL-1 core material.

pressure furnace method are described in following paragraphs.

Of the metals of primary concern in the safe operation of water-cooled reactors, namely, uranium, zirconium, aluminum, and stainless steel, only stainless steel could not be studied satisfactorily by the methods listed in the table. The difficulty resulted from an apparent intergranular reaction and the evolution of a volatile species that caused the sample to crumble at about 1500°C . This thwarted the use of any method involving direct induction heating.

In a further attempt to characterize the stainless steel-steam reaction and to study further the reaction of aluminum with steam, a high temperature, high pressure furnace is being constructed in which the sample can be wholly

Figure V-1

HIGH PRESSURE FURNACE FOR ISOTHERMAL STUDIES OF MOLTEN METAL-STEAM REACTIONS TO 1900°C

surrounded by an alumina tube which is heated to as high as 1900°C by an external tantalum resistance wire. In order to study the recently observed effect of pressure on the aluminum-steam reaction (see subsection 3, In-Pile Studies in TREAT) the furnace is being constructed to allow operation at pressures up to 1000 psi. The apparatus is shown in Figure V-1. There are two high pressure zones: an internal steam-filled zone and an external argon-filled zone. The pressure in each zone will be automatically matched to avoid stressing the ceramic tube. Crucibles containing the sample will be rapidly elevated from a moderate temperature zone where the reaction rate is negligible into the high temperature zone by an external crank mechanism. Some unreacted steam and hydrogen generated by metal-water reaction will be removed continuously from the top of the steam zone and the quantity of hydrogen will be determined as a function of time.

Studies of the isothermal aluminum-steam reaction at one atmosphere pressure by the levitation-melting method were described in a previous report (see ANL-6766, p. 101). Currently, the levitation-melting method is being applied to the study of aluminum-17 w/o uranium-2 w/o nickel alloy (SL-1 core material). This method involves the simultaneous heating and levitation of a nominal 1/4-in. dia. metal pellet in a radiofrequency field while flowing

steam over the pellet. Pellet temperature is measured and controlled by a two-color optical pyrometer. The aluminum alloy pellets were exposed to flowing steam for periods of time ranging from 5 to 100 min. The quantity of reaction was determined gravimetrically by selective dissolution of unreacted aluminum, leaving the oxide intact.

Figure V-2

REACTION OF ALUMINUM-17 w/o
URANIUM-2 w/o NICKEL ALLOY
(SL-1 COMPOSITION) WITH STEAM
USING THE LEVITATION MELTING
METHOD

The reaction of pure aluminum with steam at 1400, 1500 and 1600°C followed a linear rate law, although it may now be surmised that the initial reaction (first few minutes) was probably cubic. Subsequent cracking of the oxide film may then have led to an apparently linear reaction having the same activation energy 73.5 kcal/mole. As in the case of pure aluminum, the aluminum-uranium alloy exhibited delayed ignitions at 1600°C and immediate ignition at 1750°C (see ANL-6766, p. 102).

The need for metals inert to steam at high temperature for use in the construction of the high pressure furnace led to a limited study of the reaction of refractory metals with steam. These studies utilized a volumetric method similar to the one described in the previous report (see ANL-6766, p. 100). Small cylindrical specimens of molybdenum, rhenium, tungsten, tantalum, and niobium were supported on an alumina rod, which also acted as a sheath for a platinum, platinum-rhodium thermocouple. Specimens were heated in flowing steam by an external induction coil. Steam flowing past the sample was

Results of the levitation studies are given in Figure V-2. The results, although scattered somewhat, show reasonable agreement with a cubic rate law (slope of 1/3 on the log-log plot). The constants of the cubic rate law were obtained by considering not only the aluminum-uranium-nickel alloy data but also previous data for pure aluminum. The following rate law was obtained:

$$w^3 = 4.0 \times 10^9 t \left[\exp - \frac{73,500}{RT} \right] \quad (1)$$

where

w = metal reacted, mg Al/sq cm

t = time, min

R = gas constant, 1.987 cal/(mole) (°K)

T = temperature, °K

Equation 1 also shows limited agreement with results for the pure aluminum-steam reaction at 1200 and 1300°C.

condensed and the hydrogen produced by reaction was determined as a function of time.

The rates of the reactions of steam with the refractory metals were too high at temperatures above 1200°C to allow the use of these metals as high temperature structural materials.

Figure V-3

LINEAR RATE CONSTANTS FOR
THE MOLYBDENUM-STEAM
REACTION (1100-1700°C)

The molybdenum-steam reaction was studied in greater detail than the reactions with the other structural materials because it served as an example of a metal which oxidized by the formation of a volatile oxide. The molybdenum-steam reaction followed a linear rate law. Rate constants as a function of reciprocal temperature are plotted in Figure V-3. The metal surface acquired only a slight tarnish. The principal oxide formed was found by X-ray analysis to be the volatile MoO_3 . Overall stoichiometry as determined by comparison of the metal weight loss and the quantity of hydrogen generated indicated the formation of $\text{MoO}_{2.85}$. The stoichiometry was consistent with the slight blue color of the condensed oxide, indicating the presence of polymeric suboxides.

2. Nonisothermal Reaction Studies

The principal nonisothermal method of studying metal-water reactions has been the condenser discharge method. In these studies, wires of zirconium, uranium, and

stainless steel have been heated, almost instantaneously, in a water environment by a surge current from a bank of condensers. A disadvantage of this method has been the lack of independent control over the temperature reached by the metal and the particle sizes produced as the molten wire broke up. Moreover, the method does not allow the physical behavior of individual particles to be observed. In spite of these shortcomings it has been possible, by inference, to evaluate the separate effects of particle size, temperature, and pressure on the zirconium and uranium reaction with water. It was not

possible to study the aluminum reaction because aluminum wires could not be uniformly heated. The results with stainless steel have not been fully interpreted as yet, because corroborating isothermal data are lacking.

Because of the shortcomings of the condenser experiment, a new method of study is being developed in which single particles of the material under study are heated by irradiation from a ruby laser. The essential features of the laser experiments are illustrated in Figure V-4. A small square

Figure V-4

DIAGRAM OF EXPERIMENTAL
ARRANGEMENT FOR STUDIES OF
METAL-WATER REACTIONS BY
THE LASER HEATING METHOD

of metal foil, 1 or 2 mm on edge and 0.03 to 0.13 mm (1 to 5 mils) thick, is placed under water and is located just above a fused silica, optically flat window. The foil is heated by a laser beam, the focus of which is normally adjusted so that the energy of the beam is distributed as evenly as possible across the face of the specimen. Two kinds of experiments have been performed in which the specimen is located either in a tube open to the atmosphere or in a closed cell. The latter experiments are performed so that the minute quantities of hydrogen that are formed by the metal-water reactions can be collected and the quantity determined by microanalytical methods.

Preliminary experiments have shown that foils of uranium, zirconium, aluminum, stainless steel, and platinum can be melted by the laser beam and that the foil square is converted to a spherical particle.

The extent of reaction determined by hydrogen analyses for several experiments with zirconium and aluminum specimens is given in Table V-2. In addition to hydrogen analyses, the extent and character of the reactions are determined by metallographic examination of the oxidized particles. A photomicrograph of a zirconium sphere and an aluminum sphere are shown in Figure V-5. The oxide coating is clearly visible on the zirconium sphere, whereas the oxide coating on the aluminum particle could not be seen. The voids within the spheres were probably formed as the particles cooled from the molten state.

Two methods of studying the reaction rate, as distinguished from the total extent of reaction, are under development. One of these involves the determination of the temperature-time history of the particles by means of a two-color optical pyrometer. This device uses a combination of optical filters and two photomultiplier tubes to produce an oscilloscopic display of

Table V-2

EXTENT OF METAL-WATER REACTION OF ALUMINUM AND ZIRCONIUM
PARTICLES HEATED UNDER WATER BY A FOCUSED LASER BEAM

<u>Run No.</u>	<u>Laser Output (joules)</u>	<u>Estimated^a Temperature (°C)</u>	<u>Percent^b Reaction</u>
Aluminum (~370 μ spheres)			
L-31	10.4	--	7.3
L-29	17.8	--	6.8
L-26	25.2	--	10.5
L-27	28.7	--	7.4
Zirconium (~630 μ spheres)			
L-30	18.8	1850	31
L-25	24.7	2700	32
L-28	31.6	3600	33

^a Based on laser energy required for melting; this method was not satisfactory for aluminum, because of difficulty in determining the threshold of melting.

^b Based on hydrogen analysis.

the light emitted from the particle at two wavelengths. The other method uses high speed photography to record the rate of growth of the steam-hydrogen bubble surrounding the heated particle. It is anticipated that this information will yield important data which can be compared with calculations of steam formation rates and rates of metal-water reaction. Rates of steam formation alone will be determined using inert metals such as platinum.

3. In-Pile Studies in TREAT

The reactions of specimens of typical reactor fuel in a water environment are being studied by subjecting the fuel to a burst of neutrons in TREAT. A stainless steel autoclave contains the specimen and the water. Extent of metal-water reaction is determined by measuring the quantity of hydrogen evolved. Subsequently, particle sizes are determined and metallographic studies are made. The status of the TREAT studies is indicated in Table V-3. Extensive studies of fuel specimen behavior in room temperature water (20 psia helium overpressure) have been nearly completed. Some experiments have been performed in heated water with a 1000 psia steam overpressure and two runs have been completed with preirradiated fuel. Future plans include some experiments in which an attempt will be made to record the fuel break-up on motion picture film. Limited studies will also be performed with clusters of fuel specimens to determine how well single element studies can be applied to complex situations.

Figure V-5

METAL SPHERES FORMED BY LASER MELTING OF METAL FOIL SQUARES UNDER WATER

- (a) Zirconium, Particle Diameter 720μ
(Oxide Film Thickness, 42μ)
(b) Aluminum, Particle Diameter 337μ

Run L-30
(a)

100 μ

Run L-27
(b)

100 μ

Figure V-6

NUCLEAR ENERGY INPUT VERSUS EXTENT OF REACTION FOR ZIRCONIUM-URANIUM ALLOY PLATE MELTDOWN EXPERIMENTS IN TREAT

Figure V-7

ZIRCONIUM-URANIUM ALLOY FUEL SPECIMEN AFTER TREAT TRANSIENT CEN-100

(Original fuel plate was 1 in. x 0.5 in. x 0.1 in.)

Table V-3

STATUS OF IN-PILE STUDIES IN TREAT

Fuel Type	Room Temp Water (20 psia He)	Heated Water 285° C (1000 psia)	Preirradiated Fuel	Photographic Experiments	Large Scale Fuel Clusters
<u>Metallic</u>					
Uranium metal (including uranium-rich alloys)	Completed	2 Runs	2 Runs	Under Development	Under Development
Aluminum-rich uranium alloys	Completed	4 Runs	-	Under Development	Under Development
Zirconium-rich uranium alloys	Completed	2 Runs	-	Under Development	Under Development
<u>Cermet</u>					
Aluminum-U ₃ O ₈	4 Runs	-	-	Under Development	Under Development
Stainless steel-UO ₂	Completed	-	-	Under Development	Under Development
<u>Oxide (UO₂ or Mixed Oxide Core)</u>					
Aluminum clad	Completed	-	-	Under Development	Under Development
Zirconium clad	Completed	-	-	Under Development	Under Development
Stainless steel clad	Completed	-	-	Under Development	Under Development

Results of transient experiments conducted in TREAT with 89.35 w/o zirconium, 10.65 w/o uranium (93% enriched) alloy plates are given in Figure V-6. Most of the transients were performed in room temperature water; however, two experiments were performed in heated water at 1000 psia. The results indicated that there was no major effect of pressure or water temperature. This was in agreement with previous studies by the condenser discharge method. In most of the runs the fuel plates simply melted into the retaining crucible as shown in Figure V-7. In the most energetic run, extensive

Figure V-8

NUCLEAR ENERGY INPUT VERSUS EXTENT OF REACTION FOR ALUMI- NUM-URANIUM ALLOY PLATE MELTDOWN EXPERIMENTS IN TREAT

spattering occurred and 67.2% metal-water reaction resulted. By comparison with previous laboratory studies, it was concluded that this specimen probably reached 2600°C , at which temperature the oxide ZrO_2 is formed in a molten state and rapid particle subdivision occurs.

Results of similar experiments with aluminum-rich uranium alloy plate are given in Figure V-8. Some of these experiments were described in the previous report (see ANL-6766, p. 102). Two of the recent runs were carried out in heated water at high pressure. The extent of reaction was greatly increased in these runs. The reason for the increased reaction is under study. It is expected that laboratory studies by the high pressure furnace method will clarify the nature of the reaction.

Figure V-9

EXTENT OF METAL-WATER REACTION WITH METAL-CLAD CERAMIC CORE FUEL PINS IN TREAT MELTDOWN TESTS

Previous experiments with metal-clad UO_2 -core and mixed oxide-core fuel specimens have been extended to very high energy transient neutron bursts in TREAT. The results are presented in Figure V-9 where the experiments are correlated in terms of the calculated adiabatic temperature reached by the oxide core. It is likely that the ceramic core actually reaches the calculated adiabatic temperatures, at least in experiments at lower energies, because of the poor thermal conductivity of the oxide. The metallic cladding, however, is generally in good thermal contact with the surrounding water, so that the cladding reaches temperatures intermediate between that of the water and the ceramic. At extreme energies, the ceramic core becomes partially

vaporized and the actual temperature reached is uncertain. The relative order of the metal-water reaction for the four types of specimens is fully consistent with studies by other methods. The failure to achieve an extensive reaction with aluminum indicates that the cladding did not reach the ignition temperature of 1750°C.

Figure V-10
COMPARISON OF THE EXTENT OF
METAL-WATER REACTION WITH
PREIRRADIATED AND UNIRRADI-
ATED URANIUM FUEL SAMPLES
IN TREAT MELTDOWN TESTS

Fuel Composition: 93.5 w/o U (20%
enriched), 5 w/o
Zr, 1.5 w/o Nb
Burnup: 1.6% of U^{235} present

The results of recent reactor transient experiments with preirradiated uranium alloy fuel are compared with previous results with unirradiated fuel in Figure V-10. The alloy used in these studies contained 93.5 w/o uranium (20% enriched), 5.0 w/o zirconium and 1.5 w/o niobium. In the preirradiated specimens, 1.6% of the U^{235} atoms had been fissioned. The specimens were cooled for approximately two years. The results indicated that, at this level of burnup, preirradiation had no effect on the metal-water reaction (see Figure V-10).

4. Calculational Studies

Calculational studies include mathematical comparison of experimental results obtained from different methods and the development of techniques for accident analysis. One of the accomplishments in this area of the program has been the correlation of the extent of aluminum-water reaction found in TREAT experiments with that in the final

destructive test of the Spert-1 reactor and the accident which destroyed the SL-1 reactor. Both of these incidents were short period (3-4 msec) nuclear excursions which resulted in extensive melting of aluminum-clad, aluminum-uranium alloy fuel plates. The calculations were based on the experimental curves given in Figure V-8. An estimate of the temperatures actually reached by fuel specimens in the TREAT studies are given in the figure. These and the corresponding extents of reaction were used in the calculation. The nuclear analysis of the incidents gave an estimated peak center temperature of 1250°C for the Spert-1 experiment and 1700°C for the SL-1 accident. It was then possible to mathematically segment the reactor cores and estimate the quantity of metal reaching various temperatures. The calculations for the

SL-1 accident are given in Table V-4. The total extent of reaction was obtained by summing the expected reaction of each segment based on the results in TREAT. Estimates of the extent of the aluminum-water reactions were also obtainable from reports on the post-incident investigations of the Spert-1 test and the SL-1 accident. These estimates were based on an analysis of the α -alumina in the remains of the reactors. From these reports it was estimated that 3 to 4 Mw-sec of chemical energy was generated in the Spert experiment and 24 ± 10 Mw-sec in the SL-1 accident. Calculated values from the analysis based on the TREAT experiments were 2 Mw-sec for Spert and 26 Mw-sec for SL-1.

Table V-4

CALCULATION OF EXTENT OF ALUMINUM-WATER REACTION IN THE SL-1 EXCURSION

(Based on 60 kg of molten core material)

Temperature Reached (°C)	Energy Density (cal/g)	Relative Distance From Reactor Center ^a x	Relative Volume of Metal Within Sphere x ³	Weight of Metal within Sphere of Radius x, W (kg)	Differential Weight ^b ΔW (kg)	Percent Reaction	Metal Reacted (kg)
1700	500	0	0	0	-	-	0
1600	474	0.093	0.0008	0.048	0.048	19.9	0.010
1500	448	0.186	0.0066	0.395	0.347	17.2	0.060
1400	422	0.279	0.023	1.39	0.99	11.0	0.109
1300	396	0.372	0.051	3.06	1.67	11.0	0.184
1200	368	0.472	0.105	6.29	3.23	11.0	0.355
1100	342	0.564	0.180	10.8	4.5	7.0	0.315
1000	316	0.658	0.284	17.0	6.2	3.4	0.211
900	290	0.750	0.422	25.3	8.3	1.2	0.100
800	264	0.843	0.600	35.9	10.6	0.6	0.064
700	238	0.935	0.817	48.9	13.0	0.2	0.026
660	220	1.000	1.000	60.0	11.1	0.1	0.011
Total metal reacted							1.445

$1.445 \text{ kg} \times 18 \text{ Mw-sec/kg} = \underline{\underline{26.0 \text{ Mw-sec}}}$ chemical energy release

^a The distance x is zero at the reactor center and unity at the edge of the molten portion of the core.

^b Weight of core material that reached temperatures between 1600 and 1700°C, 1500 and 1600°C, etc.

Another phase of accident evaluation which is in progress is the estimation of the explosive pressures developed during violent nuclear excursions. This involves the calculation of the rate of steam formation by heat transfer as well as the rate of hydrogen generation by prompt metal-water reaction.

B. Metal-Oxidation and Ignition

The increased handling of reactor metals and the operation of more power reactors requires greater understanding of the hazards caused by reaction of the metals with the atmosphere. The oxidation, ignition, and burning of uranium, zirconium, and plutonium are being studied in order to clarify the factors governing the pyrophoric characteristics of these metals. This knowledge should be instrumental in reducing the hazards associated with shipping, fabricating, and processing of these nuclear reactor materials.

Three programs are presently being pursued. Two of these, plutonium oxidation and ignition studies and the determination of the thermal conductivity of uranium and zirconium powders, are nearly complete. The third, the study of the ignition of preirradiated uranium, is in progress.

1. Plutonium Oxidation Studies

Studies of the isothermal oxidation of plutonium and plutonium alloys have been carried out using a recording thermobalance located in special glovebox facilities. Preliminary oxidation data, reported previously (see ANL-6766, p. 107), showed that the reaction was linear in the temperature range from 120 to 240° C. More detailed studies, however, have indicated that the reaction initially follows a parabolic rate law from 120 to 560° C. After the relatively short period during which the oxide film formed on the metal is protective (parabolic law), the reaction rate becomes linear. Rate constants for the initial parabolic stage are plotted in Figure V-11, and those for the linear second stage of the reaction are plotted in Figure V-12. It is apparent from the figures that there is a minimum in both the parabolic and the linear reaction rates at about 400° C. This, in effect, divides the reaction into two regimes, a high temperature regime and a low temperature regime. Phase studies of the plutonium-oxygen system by Chikalla¹ et al., have shown that below 300° C there is a two-phase region consisting of $\text{PuO}_{1.62}$ and $\text{PuO}_{1.98}$, whereas between 300 and 650° C it consists of $\text{PuO}_{1.7}$ and $\text{PuO}_{1.98}$. The decrease in the rates of oxidation at the higher temperatures may result from the presence of the $\text{PuO}_{1.7}$ phase.

A rapid final stage in the reaction was reported previously to occur between 120 and 200° C. This reaction stage has now been found to result from the presence of moisture in the air or oxygen used in the experiments,

¹ Chikalla, T. D., McNeilly, C. E., and Skavdahl, R. E., The Plutonium-Oxygen System, HW-74802, 1962.

Figure V-11

PARABOLIC RATE CONSTANTS FOR THE INITIAL STAGE OF THE OXIDATION OF PLUTONIUM

high temperature regime above 400°C, ignition did not occur until about 500°C.

and does not occur if moisture is carefully excluded (~ 5 ppm H_2O) from the oxidizing gas.

2. Plutonium Ignition Studies

Ignition temperatures of cube and foil specimens of plutonium and several plutonium alloys were determined by the burning-curve method in oxygen and in air. In this method, the sample is heated at a uniform rate (usually 10 deg/min) in a flowing atmosphere of the oxidizing gas. As the rate of reaction increases, the sample self-heats and finally ignites. The temperature at which ignition occurs is determined by a graphical method. Experimental results are summarized in Figure V-13. It is apparent that there are two regimes of ignition for pure plutonium and for most of the binary alloys studied. Foil specimens (high specific area) ignited at low temperatures (about 300°C) at which the low temperature oxidation regime is operative. More massive specimens (low specific area) did not ignite in the low temperature regime. Because of the decreased rate of oxidation in the

3. Thermal Conductivity of Metal Powders

An investigation of the thermal conductivity of metal powders has been initiated to better understand powder ignition phenomena. Previous ignition studies with uranium and zirconium powders have been interpreted in terms of the Frank-Kamenetskii theory of thermal explosions. An important parameter in this theory is the thermal conductivity of the reacting medium. It was therefore important to determine experimentally how the thermal conductivity varied with particle size, temperature, and particularly, with the extent of prior surface oxidation.

A transient line source method was chosen as the experimental procedure. The line source was constructed from 25-mil diameter hypodermic tubing by placing a single constantan heating wire and two 40-gauge thermo-

Figure V-12

LINEAR RATE CONSTANTS FOR THE OXIDATION OF PLUTONIUM

couples within the tubing. The tubing was located at the center of a stainless steel cylinder which contained the metal powder. The temperature, pressure, and gas composition within the container could be varied over wide ranges. The experimental procedure was to generate heat electrically at a constant rate within the line source and to follow the transient temperature of the source continuously. The temperature depends on the rate at which heat can be removed from the source through the powder bed. Equations yielding the thermal conductivity from transient temperature data are available.

Typical results showing the effect of extent of prior oxidation and particle size on the thermal conductivity of spherical uranium powders are given in Figure V-14. The results show that the thermal conductivity at first decreases rapidly as an oxide film is formed on the particles and then more slowly as the composition approaches that of pure oxide. Studies with zirconium

powder and the analysis of the data are in progress.

Plans for Future Work

During the past year it has been decided to expand the program to include studies of the dynamics of major reactor accidents. Although the program will continue to be oriented primarily toward accidents involving chemical reaction, other energy and pressure generating processes, such as steam explosions, will also be studied. The goal of the program will be to achieve more complete analyses of actual and hypothetical meltdown accidents. Considerations in the past have been limited to thermal reactors in which water is used as the coolant and moderator. A program is currently being formulated to study safety problems associated with fast reactors, which are generally cooled with molten sodium. The metal-oxidation and ignition program is being de-emphasized as a result of the increased emphasis on accident analyses.

Figure V-13

EFFECT OF ADDITIVES ON IGNITION BEHAVIOR IN AIR OF PLUTONIUM

(Each Curve Labeled with Additive Element Present, at 2 a/o conc)

Figure V-14

THERMAL CONDUCTIVITY OF OXIDIZED URANIUM POWDER

(760 mm nitrogen, 24° C)

VI. ENERGY CONVERSION

Methods of converting nuclear energy into electricity are being studied. The main effort is being directed toward the development of regenerative emf cells. The thermocouple effect has also been investigated in a limited program. Current work on this method consisted mainly of collecting data needed to round out the program, which is being terminated.

A. Regenerative Emf Cells

Work was continued on the development of regenerative emf cells for the conversion of reactor heat into electrical energy. Such devices would operate continuously in a closed Carnot cycle, subject to Carnot efficiency limits for the overall conversion of heat to useful energy. The maximum Carnot efficiency, Eff , is given by the equation

$$Eff = \frac{T_2 - T_1}{T_2}$$

where T_1 is the cell operating temperature at which the isothermal and, as nearly as possible, reversible formation of the cell products occurs; and T_2 is the high temperature at which isothermal regeneration of the cell reactants from the cell product is accomplished. In one of the two adiabatic steps of the Carnot cycle, the cell product is transferred to the regenerator; in the other adiabatic step, the cell reactants are returned to the emf cell. The cell products regenerated at the high temperature T_2 must be separated before they are returned to temperature T_1 , where spontaneous recombination would otherwise occur with the resulting loss of all useful electrical energy. The upper practical limit of T_2 is generally considered to be about 1000°C . This limit, however, is subject to continuous re-evaluation, since it merely reflects the availability of suitable container material.

Two main types of regenerative emf cells are being studied. These are bimetallic concentration cells and the hydride cell.

The bimetallic cells have two liquid metal electrodes in contact with a molten salt electrolyte which contains only the salts of the anode metal. The anode metals under consideration are lithium and sodium. The overall reaction of these cells is

The hydride cell consists of an anode of molten metal, an electrolyte of molten salts containing the anode metal ion, and a hydrogen gas cathode. In cell operation, the liquid anode metal is oxidized to ions of the metal and the hydrogen gas is reduced to hydride ions. Currently, only two hydrides, lithium hydride and calcium hydride, are of practical interest as reactants in regenerative cells.

The known bimetallic cells offer a wide range of atomic interaction energies so that it is possible to select systems for study with regeneration temperatures ranging from about 2000°C to about 800°C and for cells with voltages ranging from about 2.0 volts to about 0.5 volt. The hydride cells do not offer this flexibility in operating range.

1. Bimetallic Cells

Many of the alkali metals react strongly with the more noble metals. However, lithium is the alkali metal of first choice for bimetallic cells for several reasons. Lithium has a low equivalent weight. Its small atomic size and its relatively stable intermetallic compounds give rise to higher cell voltages. Lithium also has a lower solubility in its fused halides than any of the other alkali metal-alkali halide systems. This is advantageous, since a high metal solubility would result in an irreversible transfer of the alkali metal to the cathode and also in an increased electronic conductance in the electrolyte. Based on the above considerations, sodium and potassium are second and third choices, respectively, for use as anode metals. Rubidium and cesium would almost certainly not be applicable to bimetallic cell operation.

In conjunction with the investigations of bimetallic cells, the solubility of intermetallic species in alkali halide fused salt media was discovered for the first time during the past year.

a. Thermodynamics of Binary Metallic Systems

Lithium-Bismuth System. Systematic studies to determine the thermodynamic properties of lithium-bismuth alloys in the temperature region between 775 and 1150°K have been concluded and data analysis has been completed.

Information used for the calculation of thermodynamic properties came from temperature-cell potential-composition studies and concerned three types of cells:

Type 1: $\text{Li}(\ell)/\text{LiCl-LiF/Li in Bi}(\ell)$ (X_{Li} = atom fraction Li);

Type 2: $\text{Li}(\ell)/\text{LiCl-LiF/Bi}(\ell)$ saturated with $\text{Li}_3\text{Bi(s)}$; and,

Type 3: $\text{Bi}(\ell)$ saturated with $\text{Li}_3\text{Bi(s)}/\text{LiCl-LiF/Li in Bi}$
(X_{Li} = atom fraction Li).

The characteristic properties of the cell of Type 1 were calculated from data obtained from laboratory studies of cells of Type 2 and Type 3. The behavior of Type -1 cell was such that, in temperature cycling, small irreversible transfers of lithium to the cathode resulted in substantial errors as a result of the unknown lithium content of the cathode.

From the calculated properties, a least-squares-derived equation relating the excess chemical potential of lithium in the lithium-bismuth alloy with temperature and composition for the region studied was found to be as follows:

$$\Delta\mu_{\text{Li}}^{\text{E}} = 9397 + 18.16 T - 0.0109 T^2 + (7103 - 19.44 T + 0.0068 T^2) X_{\text{Li}},$$

cal/mole.

This equation may be used directly to calculate other relative partial molal thermodynamic properties for lithium in the alloys (see Figure VI-1). By application of the Gibbs-Duhem relationship, it was possible to calculate the same quantities for bismuth.

Figure VI-1

EXCESS CHEMICAL POTENTIAL
OF Li IN Li-Bi, CALCULATED
FROM LEAST-SQUARES FIT OF
DATA TO:

$$\Delta\mu_{\text{Li}}^{\text{E}} = (a_1 + a_2 T + a_3 T^2) + (b_1 + b_2 T + b_3 T^2) X_{\text{Li}}$$

The standard free energy of formation of $\text{Li}_3\text{Bi(s)}$ was obtained as a function of temperature (see Figure VI-2) from the calculated partial molal free energy of bismuth and the reference electrode characteristics. The estimated error in ΔF_f° is 0.9 kcal/mole.

Using the calculated partial molal properties of lithium and bismuth, it is possible to make an estimate of the partial vapor pressures of lithium and bismuth over an alloy at higher temperatures. When such an extrapolation is made, even though its validity may be doubtful, the partial pressure of lithium over a 0.60 atom fraction lithium alloy with bismuth at 1273° K is estimated as 0.15 mm Hg. This indicates that the partial pressure of lithium may be so low that separation of any sub-

stantial quantity of lithium vapor would be difficult. Further, the vapor separated would contain considerable bismuth. Since the lithium-bismuth cell would be difficult to regenerate thermally, other systems which might be easier to regenerate are being investigated. Some of these systems are described below.

Lithium-Tin System. Studies of the cell of Type 4:

$\text{Li}(\ell)/\text{LiCl-LiF/Sn}(\ell)$ saturated with $\text{Li}_5\text{Sn}_2(\text{s})$

Figure VI-2

STANDARD FREE ENERGY OF FORMATION OF $\text{Li}_3\text{Bi(s)}$

with an overall cathode composition of 0.70 atom fraction lithium have produced cell potential-temperature data which have indicated that the liquidus temperature (1003°K) is higher than that obtained from the published phase diagram (982°K).¹

Further studies designed to resolve the difference in liquidus temperatures and to elucidate the thermodynamic properties of the binary lithium-tin system have been completed. Thermal analysis of a lithium-tin sample containing 0.70 atom fraction of lithium indicates the solid-liquid equilibrium temperature to be 991°K . Potential measurements with a cell of Type 5:

$\text{Sn}(\ell)$ saturated with Li_5Sn_2 (s)/ $\text{LiCl-LiF/Bi}(\ell)$ saturated with $\text{Li}_3\text{Bi(s)}$ indicate the liquidus equilibrium (overall cathode composition: 0.70 atom fraction lithium) temperature to be 993°K . These are considered to agree satisfactorily, but are lower than the value obtained from studies of a Type-4 cell. The liquidus temperature obtained with this cell is probably high due to an irreversible transfer of lithium from the anode to the cathode.

Cells of a different type (Type 6):

Li in $\text{Sn}(\ell)$ (X_{Li} = atom fraction Li)/ $\text{LiCl-LiF/Bi}(\ell)$ saturated with $\text{Li}_3\text{Bi(s)}$ have been operated at various values of X_{Li} between 0.10 and 0.70, and cell potential has been measured for each composition at various temperatures between 767 and 1117°K . At the higher concentration of lithium in the anode, solid Li_5Sn_2 was present at temperatures below 993°K . Using the voltage-temperature curve previously determined for the Type 2 cell:

 $\text{Li}(\ell)/\text{LiCl-LiF/Bi}(\ell)$ saturated with $\text{Li}_3\text{Bi(s)}$

data obtained with cells of Type 6 were treated to yield values which would be applicable to cells of Type 7:

 $\text{Li}(\ell)/\text{LiCl-LiF/Li}$ in $\text{Sn}(\ell)$ (X_{Li} = atom fraction Li).

Curves were plotted from these values and are shown in Figure VI-3. A thermodynamic analysis of these data is in progress.

¹ M. Hansen and K. Anderko, Constitution of Binary Alloys, p. 316, McGraw-Hill (1958).

Figure VI-3

POTENTIAL-TEMPERATURE CURVES FOR THE CELL

$$\text{Li}(\ell)/\text{LiCl-LiF/Sn}(\ell)\text{w. } X_{\text{Li}} \text{ Atom Fract. Li}$$

High Temperature Reference Electrode Studies. Cells of Type 2 have been operated successfully in the temperature region between 775 and 1150° K. In view of the potential utility of the cathode as a reference electrode in the study of alloys involving lithium as a component, it is desirable to extend the temperature range of operation of this cell to 1273° K. Two attempts to operate cells of Type 2 in this higher temperature region were unsuccessful; the cell emf decreased in an irregular manner, evidently because of massive transfer of lithium between the anode and cathode.

At temperatures between 973 and 1273° K, samples were taken of LiCl-LiF eutectic in equilibrium with an alloy of 0.70 atom fraction lithium in bismuth. These samples, which were taken in stainless steel sampling buckets, were analyzed for lithium and bismuth content. Lithium analysis consisted of an acid titration in aqueous solution, whereas bismuth was determined by a tracer technique. The average ratio of Li/Bi was found to be 3.0 ± 0.1 . This result suggested that Li_3Bi may be in the solution as a molecular entity.

The transfer of lithium from the anode makes the experimental emf data needed for the standardization of the reference electrode unreliable, and studies of the cell for this application have been discontinued.

b. Solubility of Intermetallic Compounds in Fused Salts

Following the initial observation of bismuth in the electrolyte of the lithium-bismuth bimetallic cell, a more systematic study of the solubility of lithium and bismuth in the LiCl-LiF eutectic was undertaken. The

solubility of high-purity activated bismuth (bismuth-210) in the LiCl-LiF eutectic salt mixture was measured at 600, 700, 800, and 900°C and was found to be 1.6×10^{-5} , 2.9×10^{-5} , 3.6×10^{-5} , and 3.2×10^{-5} mole percent, respectively. The liquid bismuth metal in equilibrium with the fused lithium salts gave colorless solutions.

The solubility of bismuth and lithium metal in the lithium chloride-lithium fluoride eutectic salt mixture was measured over the temperature range 600 to 1000°C after equilibrating the fused salt with a saturated bismuth metal - $\text{Li}_3\text{Bi(s)}$ solution. These data are shown in Table VI-1 as

Table VI-1

LITHIUM AND BISMUTH METAL SOLUBILITIES FOUND IN FUSED LiCl-LiF EUTECTIC SALT MIXTURE EQUILIBRATED WITH 0.70 ATOM FRACTION Li IN Bi

Temperature (°C)	w/o Li ^a	w/o Bi ^b	Atom Ratio Li:Bi
600	0.0322 ± 0.0005	0.314 ± 0.004 0.259 ± 0.05 ^c	3.09 ± 0.06
700	0.098 ± 0.002	0.968 ± 0.012 0.64 ± 0.05 ^c	3.03 ± 0.06
800	0.207 ± 0.003 0.223 ± 0.003 ^c	2.19 ± 0.03 2.16 ± 0.04 ^c	2.84 ± 0.06
900	0.380 ± 0.006	3.74 ± 0.05	3.05 ± 0.07
1000	0.957 ± 0.014	10.01 ± 0.13	2.88 ± 0.06
average Li:Bi ratio			3.0 ± 0.1

^a Hydrolysis and titration with a standard hydrochloric acid solution.

^b Bismuth containing Bi²¹⁰ tracer at a known specific activity was used in making the alloy.

^c Results of first experiment.

weight percent metal and also in Figure VI-4 as mole percent Li_3Bi versus $1/T, ^\circ\text{K}$. These saturated solutions were deep red in color. When diluted with fused salt they became orange, then yellow in color.

Figure VI-4

SOLUBILITY OF Li_3Bi IN LiCl-LiF EUTECTIC SALT MIXTURE

The absorption spectrum of the solution held in a synthetic sapphire cell was measured at 525°C in the range 5000 to $30,000\text{ cm}^{-1}$. The spectrum was characterized by an intense absorption band whose long wave length edge was located at 2 eV ($16,300\text{ cm}^{-1}$). Preliminary studies of the temperature shift of the band show that it shifts about 0.1 eV to lower energies for each 100°C rise in temperature.

The absorption spectra of lithium metal in lithium chloride² and bismuth metal in bismuth tri-chloride³ have been reported. Both systems show maximum absorption at $\sim 18,000\text{ cm}^{-1}$.

The absorption spectrum of Li_2Te dissolved in LiCl-LiF eutectic mixture was measured in a quartz cell. Below about 700°C , Li_2Te solutions do not attack quartz container vessels at appreciable rates. The ab-

sorption spectrum, determined at 600°C , revealed a single maximum at $\sim 21,000\text{ cm}^{-1}$. Exploratory experiments on alloys of lithium, sodium, potassium, and magnesium with cadmium, lead, tellurium, and selenium indicate that the solubility of intermetallic compounds appears to extend to a large variety of alkali and alkaline earth compounds with the more noble metals and metalloids. Thermodynamic stability of the salts with respect to reduction by the intermetallic compound is usually only possible with the common ion alkali or alkaline earth halides, and low melting mixtures of these are used as the solvents for intermetallic species. Many of the solutions appear to be colored.

c. High Temperature Liquid-Vapor Phase Equilibria

A number of aspects of the regeneration of a bimetallic cell have been under study. The work has been concerned with the systems Li-Bi , Li-Sn , Rb-Bi , Na-Bi and Na-Sn . The quantities under investigation have been the relative vapor pressures of the components at a given temperature and the degree of separation of components that is achieved by an equilibration over

² J. P. Young, *J. Phys. Chem.*, **67**, 2507 (1963).

³ C. R. Boston, G. P. Smith, *J. Phys. Chem.*, **66**, 1178 (1962)

a temperature gradient.

Mass spectrometric information on the Li-Bi and Rb-Bi systems was obtained in cooperation with J. Berkowitz* and W. Chupka*. The Li-Bi system study was done on the compound Li_3Bi . Over the temperature range from 970 to 1130°K, the predominant vapor species were Li^+ and Bi^+ ions. LiBi^+ molecule ions were first detected in small quantity at 1072°K. At most, the peak height of LiBi^+ was 0.6% of that of Bi^+ , and occurred at 1100°K. Other species, which were first detected in small amounts at 1083°K, were Bi_2^+ and LiBi_2^+ ; for example, at 1106°K, the peak height of LiBi_2^+ was 0.04% of that of Bi^+ . From these results, it appears that Li_3Bi evaporates predominantly by decomposition. This aspect is favorable for thermal regeneration of a Li-Bi regenerative cell since it indicates that Li_3Bi , the most stable entity in the Li-Bi system, can be thermally decomposed. However, from a practical standpoint, a functioning cell would require that the components, both of which would be in the vapor phase at regeneration, be separated. This separation would be rather difficult in view of the closeness of the normal condensation points of lithium and bismuth vapors, namely, 1336 and 1560°C, respectively.

Thermodynamic data were derived from the mass spectrographic work on Li_3Bi . By a second law treatment of relative vapor pressures, ΔH for the reaction $\text{Li}_3\text{Bi(s)} \rightarrow 3 \text{Li(g)} + \text{Bi(g)}$ was found to be -192 kcal/mole at 1050°K. From determination of absolute vapor pressures in experiments in which a sample was vaporized completely, a value of -93.9 kcal/mole was obtained for the free energy change for the above reaction. Using known free energies of vaporization for lithium and bismuth, the free energy for the reaction

at 1120°K was determined to be +46.0 kcal/mole. This is in good agreement with the extrapolated emf-derived value of +43.2 kcal/mole.

The Rb-Bi system was examined mass spectrographically using the compound Rb_3Bi . The data which were collected could be interpreted only semi-quantitatively. It was concluded that Rb_3Bi also evaporates by decomposition, and that only about 2% of the bismuth vaporizes during the time required to vaporize 90% of the rubidium. The initial rate of rubidium volatilization (at about 700°K) was considerably greater than that of bismuth, perhaps by a factor of about 100. These results indicate that a Rb-Bi bimetallic cell should be easy to regenerate. Other factors, however, must now be recognized as arguing against adoption of such a cell, the two main ones being the high solubility of rubidium in its fused halides and the relatively low cell voltage.

* Physics Division, Argonne National Laboratory

Experiments more closely approximating actual regeneration were done in which a possible cell product alloy was allowed to decompose at a high temperature and to equilibrate with the condensed (regenerated) material at a lower temperature. This was accomplished in a sealed stainless steel tube in which the end containing the sample was heated to a high temperature while the other end was maintained at a lower temperature. The experiments were exploratory in nature and should not be considered definitive. However, the results are indicative of the behavior of one system relative to another. From a 50 a/o Na-Sn alloy at 950°C , 90% of the sodium originally introduced in the form of the alloy was recovered at the cooler end of the tube, which was maintained at 550°C . The tin content of the distilled sodium was 40 ppm. From a 70 a/o Na-30 a/o Bi alloy at 920°C , 48% of the sodium was collected at the cooler end (maintained at 515°C). The distilled sodium contained 2.7 ppm bismuth. A similar experiment with the Li-Sn system resulted in a recovery of 16.7 a/o of the original lithium. Experiments of greater refinement are being planned. Interest will center on the Na-Bi system, since this system promises a good balance of the various characteristics needed for a practical regenerative cell, such as good voltage, regenerability, and, probably, acceptably low solubility of anode material in the electrolyte.

In operating a lithium hydride emf cell through a regenerative cycle, it is important to keep the cell temperature as low as possible in order to maximize the Carnot cycle efficiency. Therefore, thermal analysis studies are being made of several salt systems in search for lower melting eutectics. All components in the fused salt electrolyte must, of course, be thermodynamically stable with respect to lithium metal.

Thermal analyses experiments have been completed on the LiH-LiCl system and on the LiH-LiBr system. The latter system has a eutectic composition of 29.7 m/o lithium hydride, which melts at 452.3°C . The liquid-solid equilibrium data are plotted in Figure VI-5. Within the limits of the experimental work (5 to 90 m/o LiH) solid solution formation was not observed.

An excellent outline is given by Wagner⁴ of a method for the calculation of thermodynamic functions for each component of a binary system from liquid-solid equilibrium data. In this type of analysis, only the heterogeneous equilibrium between pure solid and the binary liquid mixture is considered. These data are given in Tables VI-2 and VI-3. An integrated form of the Gibbs-Duhem equation was used to calculate the excess chemical potential of one component in the region of the other.

The lithium hydride-lithium bromide system is very similar to the lithium hydride-lithium chloride system in that deviations from ideal behavior are small and positive. Deviations of this type are indicative of the existence

⁴ C. Wagner, Thermodynamics of Alloys, Addison Wesley Press (1952).

Figure VI-5

PHASE DIAGRAM OF THE LiH-LiBr SYSTEM

Table VI-2

THERMODYNAMIC DATA FOR LiH IN LiH-LiBr SYSTEM

<u>LiH</u> <u>(m/o)</u>	<u>T_e^a</u> <u>(°K)</u>	<u>Δ_μ^M^b</u> <u>(cal/mole)</u>	<u>Δ_μ^E^c</u> <u>(cal/mole)</u>	<u>γ^d</u>
100.0	959.0	-	-	1.0
89.7	935.9	-127.3	74.9	1.038
80.0	912.2	-259.5	145.0	1.075
74.9	899.8	-329.1	187.7	1.099
70.0	886.7	-403.6	224.9	1.120
60.1	860.3	-554.6	315.9	1.172
55.0	843.2	-653.2	348.6	1.192
48.6	820.4	-786.0	390.4	1.217
40.6	786.4	-986.1	422.6	1.237
35.1	758.1	-1153.7	423.7	1.238
29.7 ^e	725.5	-1348.0	402.4	1.224

^a T_e = Liquid-solid equilibrium temperature.

^b Δ_μ^M = Relative partial molar free energy.

^c Δ_μ^E = Excess partial molar free energy.

^d γ = Activity coefficient.

^e Eutectic composition.

Table VI-3

THERMODYNAMIC DATA FOR LiBr IN LiH-LiBr SYSTEM

LiBr (m/o)	T_e^a (° K)	$\Delta \mu^M^b$ (cal/mole)	$\Delta \mu^E^c$ (cal/mole)	γ^d
100.0	820.8	-	-	1.00
95.0	811.4	-48.1	34.7	1.017
90.2	800.4	-104.1	60.0	1.031
85.0	786.7	-173.6	80.6	1.042
80.4	772.4	-245.8	88.9	1.046
75.0	751.7	-348.9	80.7	1.042
70.3 ^e	725.5	-477.6	30.7	1.016

^a T_e = Liquid-solid equilibrium temperature.

^b $\Delta \mu^M$ = Relative partial molar free energy.

^c $\Delta \mu^E$ = Excess partial molar free energy.

^d γ = Activity coefficient.

^e Eutectic composition.

of an associated species in the solution. Mass spectrometric⁵ analyses of both lithium bromide and lithium chloride vapor in equilibrium with its condensed phase shows the dimer/monomer ratio to be 2.5 to 1. It is quite likely that a similar situation exists when a nonionizing solvent such as lithium hydride is used as the solvent.

2. Lithium Hydride Regenerative Cell

The reaction in the lithium hydride cell is the oxidation of lithium metal to lithium ions and the reduction of hydrogen gas to hydride ions (see ANL-6766, p. 113). The liquid alkali metal anode is capable of supporting very high current densities. On the other hand the operation of gas electrodes is an old and classic cell problem. Very early in this work it was decided that a porous metal gas cathode would not be acceptable in a hydride regenerative cell. The difficulties encountered with porous metal cathodes were the occurrence of variable catalytic activity at the surface of the metal and alternate flooding of the porous metal by hydrogen and fused salt. Metal diaphragms (nonporous) that are known to diffuse hydrogen rapidly at relatively low tem-

⁵ J. Berkowitz and W. Chupka, J. Chem. Physics 29, 653 (1958).

peratures are platinum, palladium, and silver-palladium alloys. However, these noble metals react very strongly with lithium, and diaphragms of these noble metals rapidly disintegrate in the cell environment when in contact with the lithium salt electrolyte. Transition metals, such as iron and nickel, appear to be applicable as diaphragms, except that their diffusion rates are a factor of ten lower than desired to support cell current densities of 100 ma/cm² at about 500°C. These diaphragms appear to be compatible with the cell environment and have also the important property of not being extremely sensitive to trace impurities in the gas or cell electrolyte, e.g., iron oxide is easily reduced by hydrogen gas. The metals in groups IV and V (Tc, Zr, Hf and U, Nb, Ta) have high hydrogen solubility and permeability, but only vanadium and niobium have the required mechanical strength in a hydrogen atmosphere to function as an electrode. Niobium has been tested in cells during the past year; it was found to be extremely sensitive to impurities which reacted at the metal surface and resulted in very large decreases in hydrogen permeation rates. Also, the open circuit voltage at a H₂, H⁻, Nb electrode was 0.40 volts, which was about one-half of that found for iron or vanadium.

Vanadium metal diaphragms were also tested during the past year and were found to function very well. Contrary to the findings reported in the literature,⁶ vanadium in our experiments has proven compatible with the lithium hydride cell environment.

Permeation rates for hydrogen through vanadium shows some non-reproducible characteristics, the extent of which are shown in Figure VI-6. The literature⁷ indicates that this irregular behavior is characteristic of vanadium. With respect to hydrogen, vanadium is classified as an exothermic occluding metal; that is, a metal which absorbs hydrogen in large quantities with a negative temperature coefficient of solubility. Metals behaving in this way exhibit two unique permeation characteristics. Firstly, the metal must be "activated" at a high temperature in order to induce permeation, and secondly, if the metal is thermally cycled while charged with hydrogen, the permeability decreases with time. Reactivation can only be achieved with difficulty at a temperature higher than the initial temperature of activation. These characteristics can be interpreted as being the result of the expansion and contraction of the metal lattice and possibly surface contamination.

A lithium hydride-emf cell has been operated for 540 hours using a vanadium metal diaphragm. When operated under a resistive load, the average current density obtained was 130 ma/cm² at half open-circuit voltage and a hydrogen pressure of one atmosphere. This current density was achieved

⁶ ASD-TDR-62-241, Final Report, Electrode Development Program, TAPCO, Thompson Ramo Wooldridge Co. (1962).

⁷ Smith, D. P., Hydrogen in Metals, Chapter 3, Univ. Chicago Press, 1948.

Figure VI-6

HYDROGEN PERMEATION ISOBARS
OF 0.010-INCH THICK VANADIUM

without making any attempt to activate the diaphragm. The response of hydrogen pressure and cell voltage was studied. The slope of a plot of emf vs the logarithm of the hydrogen pressure corresponded to the expected theoretical (Nernst) slope of one, indicating the reversibility of the H₂, H⁺, V electrode. A similar result was obtained for iron, but not for niobium.

The decision concerning the practicality of the lithium hydride regenerative cell will depend largely on answers to the following questions:

(1) How high are the hydrogen gas equilibrium pressures in the regeneration step, which may involve either dilute solutions of lithium hydride in lithium metal or lithium hydride in fused salt electrolyte? This question can be answered by laboratory studies of the hydrogen gas equilibrium over solutions of lithium hydride in metal or lithium hydride in fused salts. Results of these experi-

ments will also determine whether a pump will be required to recirculate the hydrogen gas back to the cell electrode.

(2) How reliable is the performance of a given hydride, hydrogen gas diffusion diaphragm? In the case of vanadium, the performance of the diaphragm needs to be evaluated beyond the 540-hour static test that has been successfully concluded. To do this, cells with circulating fused salt electrolyte and liquid lithium metal anode need to be operated under heavy current loads for long periods of time (>1000 hr). This testing would be best suited to engineering studies.

B. Thermoelectricity Research

For energy conversion devices, materials possessing high melting points and low vapor pressures are desirable if these devices are to be used in high temperature nuclear reactor systems. The lanthanide and actinide sulfide systems are highly refractory and have phases with carrier concentrations in the semiconducting and semimetallic range. Uranium sulfide, thorium sulfide, and their solid solutions have been investigated.

The results of measurements on the temperature dependency of the Seebeck coefficient and resistivity of sintered specimens of uranium

Figure VI-7

ABSOLUTE SEEBECK COEFFICIENT VERSUS TEMPERATURE FOR
URANIUM MONOSULFIDE, THORIUM MONOSULFIDE, AND US-ThS
SOLID SOLUTIONS

monosulfide, thorium monosulfide, and US-ThS solid solutions indicate semi-metallic behavior for US and metallic behavior for ThS. The thermoelectric power of US (Figure VI-7) shows a weak dependence on temperature and decreases with increasing ThS content. Except for initial disordering effects, the resistivity of US and the US-ThS solid solutions (Figure VI-8) show a similar dependence on temperature and composition. With ThS, however, a linear increase in resistivity is found which is characteristic of metallic behavior, and also is consistent with the trend in Seebeck coefficient values obtained on this material, namely, an increase in Seebeck coefficient with temperature. The trend in resistivity data (Figure VI-9) with composition appears to be typical of the resistivity of disordered alloys in which a continuous range of solid solutions is formed from pure components which differ considerably in their resistivity.

The presence of higher sulfides (U_2S_3 , U_3S_5) in US results in a considerable lowering of the Seebeck coefficient with temperature (Figure VI-10). The slightly higher values obtained during the cooling cycle appear to be indicative of composition changes occurring during the measurements.

Figure VI-8

RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR SINTERED SPECIMENS OF URANIUM MONOSULFIDE, THORIUM MONOSULFIDE, AND US-ThS SOLID SOLUTIONS

Figure VI-9

ROOM TEMPERATURE RESISTIVITY VERSUS COMPOSITION FOR US-ThS SYSTEM

Figure VI-10

EFFECT OF HIGHER SULFIDES ON THE THERMOELECTRIC POWER OF URANIUM MONOSULFIDE

Using recent thermal conductivity values obtained at Argonne National Laboratory⁸ from room temperature to 1000 $^\circ\text{C}$ on a sintered specimen of uranium monosulfide ($\sim 97\%$ theoretical density), and the Seebeck coefficient and resistivity values shown in Figures VI-7 and VI-8, one can estimate figure of merit* values. The calculated figure of merit values in Table VI-4 are too low for useful high temperature power generation by a factor of approximately ten.

A cursory examination of uranium monophosphide yielded Seebeck coefficient values which were almost identical to those of US and showed the monophosphide to have a similar temperature dependency as uranium monosulfide.

The results of the work on US, ThS, and US-ThS solid solutions along with a discussion of the theoretical significance of the findings will be published in the Journal of Applied Physics.

⁸ R. J. Dunworth, Metallurgy Division, Personal Communication

* The figure of merit, Z , is a convenient parameter which characterizes useful material properties of potential semiconductors, and is defined by the equation $Z = a^2/\rho k$, where a is the thermoelectric power, ρ the resistivity, and k the thermal conductivity.

Table VI-4

FIGURE OF MERIT AS A FUNCTION OF TEMPERATURE FOR
URANIUM MONOSULFIDE

Temp (°C)	Seebeck Coefficient ($\mu\text{v}/^{\circ}\text{C}$)	Resistivity ($\mu\text{ohm-cm}$)	Thermal Conductivity ^a [watts/(cm)(deg)]	Figure of Merit (deg ⁻¹)
25	50.0	286	0.0979	0.89×10^{-4}
100	55.6	298	0.0982	1.1×10^{-4}
200	58.8	310	0.1035	1.1×10^{-4}
300	59.2	318	0.1095	1.0×10^{-4}
400	58.4	323	0.1170	0.90×10^{-4}
500	56.6	325	0.1252	0.79×10^{-4}
600	54.4	327	0.1331	0.68×10^{-4}
700	52.0	328	0.1395	0.59×10^{-4}
800	49.4	328	0.1432	0.52×10^{-4}
900	46.6	328	0.1472	0.45×10^{-4}
1000	43.5	328	0.1490	0.41×10^{-4}

^a Data of R. Dunworth, Metallurgy Division, ANL, corrected to 85% theoretical density.

VII. DETERMINATION OF NUCLEAR CONSTANTS

One of the most important numbers used in the description of the behavior of a nuclear reactor is the quantity $\eta = \nu / (1 + \alpha)$, which is the number of neutrons formed per neutron absorbed in the fissile material. Here ν is the average number of neutrons produced per fission, and α is the ratio of the capture and fission cross sections of the species in question. The net result of the capture and fission is the production of $\eta - 1$ neutrons, that is, $\eta - 1$ neutrons are available for possible breeding. The breeding ratio actually obtained is a fraction of $\eta - 1$, the value of the fraction depending upon the geometry of the reactor and the presence of neutron-absorbing materials. Taking these variables into account, the breeding ratio is written:

$$R = \eta - 1 - \frac{A + \Lambda - F(\nu' - 1)}{1 + \alpha}$$

where, for each fissile atom fissioned, A is the number of neutrons captured by parasites, Λ is the number leaking out of the system, F is the number of fertile nuclei fissioned, and ν' is the average number of neutrons per fission in the fertile species.

It is apparent that, in addition to being a function of ν and α , the breeding ratio is a function of the cross sections for processes which remove neutrons unproductively, such as radiative capture, (n, p) , and (n, α) reactions. Further, reactions which are responsible for the degradation of the neutron energy spectrum, that is, inelastic and elastic scattering, need to be studied. All of these reactions are functions of neutron energy, which, in fast reactors, range from a few kev to several Mev.

In the present program, many of the above neutron reactions have been studied for fissile and fertile species, and for other materials occurring in reactors.

A. Capture and Fission in Fissile and Fertile Materials

In ANL-6766, pp. 134-139, results were given for the capture cross sections of Th^{232} for monoenergetic neutrons between 0.18 and 1.3 Mev. Further, in that report data were given on the ratio of capture and fission cross sections of U^{233} , U^{235} , U^{238} , and Pu^{239} as a function of position in the fast breeder reactor, EBR-I, Mark III. Similar work is now in progress with the fast breeder, EBR-II. Samples of U^{233} , U^{235} , U^{238} , Pu^{239} , Pu^{240} , and Pu^{242} are being prepared for irradiation at various positions in EBR-II. Following irradiation, the samples will be analyzed for the number of fissions and captures, and the results will be compared with calculations based upon multigroup diffusion theory.

B. Radiative Capture Cross Sections

Studies of the radiative capture cross sections of structural materials, coolants, and fuel matrix materials are needed in order that the effects of these materials on the behavior of a nuclear reactor may be assessed. In recent studies, capture cross section data have been obtained for rhenium, gadolinium-158, and erbium-170. Interest in the capture cross section of rhenium relates to its several potential uses in a nuclear reactor. Rhenium has favorable high temperature properties; its metallurgical properties resemble those of tantalum and tungsten. The alloys of rhenium with tungsten are highly ductile. These alloys might be used for the fabrication of tubing or as fuel matrix material. Interest in gadolinium and erbium stems from the fact that these and some other rare earths have been proposed as possible reactor control materials.

In the present program, radiative capture cross sections of rhenium-187, gadolinium-158, and erbium-170 have been measured in the neutron energy range from a few key to about 2 Mev. Monoenergetic neutrons were produced by the reaction $\text{Li}^7(p, n)\text{Be}^7$ when protons from the Van de Graaff accelerator bombarded a lithium target. The neutron flux was measured with a fission chamber which counted fissions in a thin deposit of uranium. After neutron irradiation, the targets were analyzed for the gamma ray spectrum of the activation products by means of a NaI crystal and a multichannel analyzer. The absolute disintegration rate corresponding to the gamma spectrum of the irradiated target was determined by comparing this spectrum to that of a known activity of the same species counted in the same geometry, the activity of the latter having been determined by absolute beta counting. Results of some recently measured capture cross sections follow.

1. Capture Cross Section of Rhenium

Rhenium consists of the two isotopes, 37.07% Re^{185} and 62.93% Re^{187} . Radiative capture in rhenium produces the following reactions:

Data for all three processes have been obtained. Results are given in Figure VII-1 for the cross section for the production of both states of Re^{188} . Representative neutron energy spreads about some of the points are shown, and typical standard deviations of the cross section values are indicated. Two other datum points are shown. The point at 25 kev is the result of a measure-

Figure VII-1

NEUTRON CAPTURE CROSS SECTION OF RHENIUM-187

ment with a photoneutron source, as quoted by Hughes and Schwartz,¹ and the point at 1 Mev is the value for a fission neutron spectrum, as measured by Hughes et al.² Although data have also been obtained for the Re^{185} cross section and for the cross section for the production of the 20-min state of Re^{187} , the results are not yet in final form.

2. Capture Cross Section of Gadolinium-158

One of the gadolinium isotopes whose capture cross section can be measured by neutron activation is Gd^{158} , which constitutes 24.9% of natural gadolinium. The activation product of Gd^{158} is the 18-hr Gd^{159} . The capture cross section of Gd^{158} has been determined between neutron energies of 50 keV and 2 MeV, and the results are shown in Figure VII-2.

3. Capture Cross Section of Erbium-170

The neutron activation product of Er^{170} (natural abundance, 14.9%) is a 7.5-hr beta emitter, Er^{171} . The capture cross section of Er^{170} has been measured between neutron energies of 0.15 and 1.9 MeV, and the results are given in Figure VII-3.

¹ Hughes, D. J. and Schwartz, R. B., BNL-325, Neutron Cross Sections, 2nd Ed. (1958).

² Hughes, D. J., Garth, R. C., and Levin, J. S., Phys. Rev. 91, 1423 (1953).

Figure VII-2

NEUTRON CAPTURE CROSS SECTION OF GADOLINIUM-158

Figure VII-3

NEUTRON CAPTURE CROSS SECTION OF ERBIUM-170

C. Neutron Inelastic Scattering

The importance of inelastic scattering in the degradation of the neutron spectrum in a fast reactor was mentioned above. The inelastic scattering event leaves the target nucleus in an excited state; the neutron is emitted from the compound system with its energy decreased by an amount equal to

the energy of the excited state. The excited nucleus then returns to its ground state by the emission of a gamma ray. Generally, it is desired that in a fast reactor there be as little inelastic scattering as possible. One requires a knowledge of: (1) inelastic scattering cross sections as a function of incident neutron energy, (2) distribution of energies of the scattered neutrons, and (3) angular distribution of the scattered neutrons. Inelastic scattering can be studied by detecting either the scattered neutrons or the gamma rays, and the two types of experiments complement each other. The Reactor Physics Division has made extensive studies of the neutrons from inelastic scattering. Currently, a program is underway for the measurement of cross sections for the production of gamma rays from the reaction $(n, n'\gamma)$. This work is being carried out as a cooperative effort with the Reactor Physics Division. The 3 Mev pulsed VandeGraaff accelerator of the Reactor Physics Division is being used in the studies. Measurements for a given nucleus are being made as a function of neutron energy and as a function of the angle of emission of the gamma ray with respect to the direction of the neutron beam. These experiments will also give information on the gamma ray branching ratio for the decay of nuclear excited states, and in many cases will allow angular momentum and parity values to be assigned to these states. The program of study will include many of the typical reactor materials. Preliminary results have been obtained for the gamma rays resulting from the excitation of the first few energy levels of iron, copper, zirconium, and niobium.

D. Neutron Total Cross Sections

The neutron total cross section is a measure of the total attenuation of a neutron beam in a sample by all processes of absorption and scattering. This quantity is measured by determining the transmission of neutrons through a sample, that is, by measuring the intensity of a neutron beam with and without the sample placed in the beam. In the present program, neutron total cross sections have been measured for several of the elements which were discussed above in the section on radiative capture. The work was carried out using the Van de Graaff accelerator and associated neutron collimation and detection equipment of the Physics Division. Data are now presented for the total cross sections of rhenium, gadolinium, and holmium for neutron energies between a few kev and 2 Mev.

1. Neutron Total Cross Section of Rhenium

The total neutron cross section of rhenium between 1 kev and 2 Mev is given in Figure VII-4. Shown in the figure also are the few available points from the fast chopper data of Melkonian et al.³ The standard deviations of the cross section values range from about $\pm 1.5\%$ at the low energies to less than $\pm 1\%$ at high energy. The neutron energy spreads about the points vary from about ± 0.5 kev at low energy to ± 25 kev at high energy. In the energy

³ Melkonian, E., Havens, W. W., and Rainwater, L. J., Phys. Rev., 92, 702 (1953).

Figure VII-4

NEUTRON TOTAL CROSS SECTION OF RHENIUM

region around 1 or 2 kev, the Van de Graaff reaches its lower energy limit of usefulness for high resolution work and the fast chopper reaches its upper limit.

2. Neutron Total Cross Section of Gadolinium

Total cross sections of gadolinium are given in Figure VII-5 for neutron energies between 1 kev and 2 Mev. The figure also includes fast chopper data¹ already known in the lower energy region. The curve shows the difficulty in resolving the resonance structure in the region of a few kev, where both the fast chopper and Van de Graaff neutron sources are limited in effectiveness. The standard deviations of the present data range from about $\pm 1.5\%$ at the lowest energies to less than $\pm 1\%$ at the highest. Neutron energy spreads range from ± 0.5 kev at low energy to ± 25 kev at high energy.

3. Neutron Total Cross Section of Holmium

Total cross sections of holmium have been measured between 2 kev and 2 Mev, and the nearly structureless curve of the data is given in Figure VII-6. The standard deviations of the points and the neutron energy spreads have essentially the same values as the rhenium and gadolinium data above.

Figure VII-5

NEUTRON TOTAL CROSS SECTION OF GADOLINIUM

Figure VII-6

NEUTRON TOTAL CROSS SECTION OF HOLMIUM

VIII. ANALYTICAL CHEMISTRY

The Analytical Chemistry Group provides a broad spectrum of analytical support to the research and development groups of the Chemical Engineering Division. The group includes a large section for elemental analysis, a section for the development of new analytical methods, and sections which specialize in X-ray diffraction and spectroscopy, in gas chromatography and in radiochemistry. During the year, a new section was formed whose responsibility will be studies made with the newly acquired electron probe microanalyzer.

During the past year, the elemental analysis section used 100 methods to perform more than 13,000 analyses; the X-ray section determined several hundred diffraction patterns and performed many spectrochemical assays and identifications; the gas chromatography section analyzed numerous gas samples from glove boxes, furnaces, and calorimeters.

Research in analytical chemistry is, to a large extent, the outgrowth of the service work. As the Division's program changes, existing analytical methods must be modified or new methods developed to meet the conditions that are imposed by the nature of the samples submitted for analysis. In the majority of samples, the element of interest is only a minor constituent, and the analytical method must either tolerate or provide means for separating the constituent of interest from as much as a millionfold excess of such process materials as zinc, magnesium, salt fluxes, and aluminum oxide.

The analytical effort during the year was highlighted by determinations of the yields of technetium-99 from both thermal and fast fission of uranium-235, determination of the yield of cesium-137 from the thermal fission of uranium-235, the development of a particularly sensitive spectrophotometric method for ruthenium, the determination of the lattice constants of 13 rare earth-cadmium alloys of the CeCd_6 type, the application of gas chromatography to the analysis of helium and argon samples from glove box atmospheres, and the development of a neutron activation method for lithium.

A. Technetium-99 as a Burnup Monitor for Fast and Thermal Reactors

Of the 85 or so fission nuclides which are present in discharged reactor fuels, very few are suitable as fission monitors. The monitor must have a high fission yield, a long half-life and a low neutron cross section; it must be absent in the charged fuel but retained in the fuel during irradiation. Cesium-137 (29.1 years), the nuclide which has been used as a fission monitor to the near exclusion of all others, has been shown to be unsatisfactory for EBR-II fuel since on prolonged irradiation at the reactor's operating temperature, 600°C , the cesium diffuses out of the fuel into the sodium bond.

The establishment of technetium-99 (10^5 years) as a burnup monitor

for EBR-II as well as thermal reactors fueled with uranium-235 is now nearly complete. The technetium is separated from the other fission products and uranium by distillation of the volatile technetium septoxide from concentrated sulfuric acid; detection is made spectrophotometrically after reaction with the chromogenic reagent, dithiol. The distillation is carried out in a cave; the distillate is sufficiently decontaminated to permit color development without shielding.

Since technetium-99 is not removed in the fuel processing cycle, it cannot be used directly as a burnup monitor for recycled fuel. However, this difficulty will be circumvented by the inclusion of virgin fuel rods in each subassembly of reprocessed fuel.

Uranium samples which were irradiated in such a way that the number of fissions could be determined by other established methods have been analyzed for their technetium-99 content. When the analyses for total fissions are completed, the first direct determinations of the yields of technetium-99 from both fast and thermal fission of uranium-235 will be made.

B. Yield of Cesium-137 from the Thermal Fission of Uranium-235

Uranium samples which had undergone a known number of thermal fissions were analyzed radiochemically and mass spectrometrically for their cesium-137 content. This endeavor was prompted when wide discrepancies were found in an inter-laboratory comparison of burnup analyses and cesium-137 standards. The yield of cesium-137 from the thermal fission of uranium-235 was found to be $6.33 \pm 0.06\%$. The most-often-quoted literature value is $6.15 \pm 0.26\%$. The results of the radiochemical studies have been made available to other laboratories by the publication of results of a cross-calibration of our samples with the cesium-137 standard furnished by the American Society for Testing Materials.

C. Spectrophotometric Determination of Ruthenium

In the development of a liquid metals process for recovering uranium from EBR-II melt refining skulls (see Section I of this report), samples of zinc and magnesium-zinc which contained about 0.01% ruthenium were submitted for analysis. Reasonably precise analyses were required since the experimental objective was to determine the fate of ruthenium in the process. The sensitivity of the method then in use was not sufficient to produce results of the desired precision.

A new method which is more sensitive by a factor of 10 has been developed. The ruthenium is separated from zinc, magnesium, uranium, and from other fission constituents by distillation of the tetroxide; the tetroxide is extracted into carbon tetrachloride; a colored complex is formed by reacting the tetroxide with 1-nitroso-2-naphthol and ascorbic

acid; and the absorbance measured. For samples containing 30 μg of ruthenium, the relative standard deviation for a single determination is 1.1%.

In the development of this method for ruthenium, a particularly vexing problem was that of establishing conditions for the quantitative distillation and retention in solution of microgram amounts of ruthenium tetroxide. Ruthenium tetroxide is a very strong oxidant and reacts with minor reducing impurities rapidly, and with water more slowly, to form ruthenium (IV) ions and compounds. If particular attention is paid to the cleanliness of the still and the purity of reagents, as little as one microgram of ruthenium can now be distilled quantitatively; if sodium periodate is present as a holding oxidant in the aqueous phase during the extraction operation, the ruthenium can be transferred and maintained as the tetroxide in carbon tetrachloride. In the absence of periodate the carbon tetrachloride or an impurity slowly reduces the tetroxide.

D. X-ray Diffraction Studies of CeCd_6 Type Rare Earth-Cadmium Alloys

Investigation of the various rare earth-cadmium binary systems disclosed the existence of a compound corresponding to the composition MCd_6 in all systems except the lanthanum-cadmium system.¹ Measurements of the solubility of the rare earths in liquid cadmium led to the discovery of GdCd_6 , TbCd_6 , DyCd_6 , HoCd_6 , ErCd_6 , TmCd_6 , YbCd_6 , and LuCd_6 . Each of these compounds has been identified as the solid phase in equilibrium with saturated solutions of the particular rare earth in liquid cadmium at temperatures just above the melting point of cadmium. The compounds enumerated above were isolated from ingots used in the solubility measurements. The remainder of the MCd_6 compounds, i.e., CeCd_6 , PrCd_6 , NdCd_6 , SmCd_6 , and EuCd_6 were prepared by direct heating of a mixture of the appropriate stoichiometric amounts of each rare earth and cadmium.

X-ray diffraction powder photographs of the MCd_6 alloys were taken with a 114.6 mm Debye-Scherrer camera. All powder photographs of the alloys are similar in appearance and can be indexed on the basis of a cubic unit cell.

A plot of the mean metallic radii of the rare earth metals versus their atomic numbers is depicted in Figure VIII-1. The mean metallic radii are calculated from the lattice constants of the pure metals. Also depicted in Figure VIII-1 are the lattice constants of the MCd_6 compounds. The correspondence between (1) the mean metallic radii of the rare earth metals and (2) the lattice constants of their respective MCd_6 compounds is

¹ I. Johnson, Solubility of Rare Earth Metals in Liquid Cadmium, Proceedings of the Second Conference on Rare Earth Research, J. F. Nachman and C. E. Lundin, eds., Gordon and Breach, New York, 1962, p. 125.

Figure VIII-1

RARE EARTH MEAN METALLIC RADII AND MCd_6 LATTICE CONSTANTS

evident. A consequent conclusion is that with the exception of europium and ytterbium, the rare earth metallic valences in this study are three or nearly three, while the metallic valences of europium and ytterbium are more nearly two.

E. Gas Chromatography

A number of the research and development programs being conducted within the Division require the use of highly purified inert atmospheres. The need to verify and monitor the purity of these special atmospheres, particularly for moisture, oxygen, and nitrogen, caused the Analytical Chemistry Group to initiate work on gas analysis.

Moisture determinations are being made with commercially available electrolytic hygrometers. These instruments have proved to be very satisfactory. They are highly sensitive, simple to operate, easy to maintain, and will monitor continuously.

Gas chromatography is being used to monitor inert atmospheres for oxygen and nitrogen. For helium samples, the columns are packed with Molecular Sieves and are operated at room temperature; helium is used as the carrier gas; and detection is made by means of a commercial hot-wire thermal conductivity detector. To achieve the desired sensitivity for nitrogen and oxygen, additional amplification, the use of a very sensitive recorder, and careful thermostating of the detector were required. With this system, the detection limits for oxygen and nitrogen are 0.3 and 0.5 ppm, respectively.

The same column, carrier gas, and detector are being used for argon samples but the sensitivities for oxygen and nitrogen are only 200 and 10 ppm, respectively. Not only are oxygen and argon difficult to separate, but also their thermal conductivities are nearly the same. Detectors which rely on other physical properties for sensing are being investigated. Until the problem is resolved, oxygen concentration is being determined by a commercial instrument which uses an electrochemical cell. (The cell employs a silver-cadmium electrode system in a potassium hydroxide electrolyte. The current from this cell is a function of the concentration of dissolved oxygen.) This instrument is not particularly satisfactory since its high-to-low response is very slow and the instrument is difficult to maintain.

F. Determination of Lithium by Neutron Activation

The need for lithium analysis of samples which contain plutonium prompted the development of an activation method. (In the absence of plutonium, lithium would ordinarily be determined by flame photometry.) After the bulk of the plutonium has been separated by extraction into tributyl phosphate or absorption onto an anion exchange resin, a dilute nitric acid solution of the lithium is irradiated with thermal neutrons. Two nuclear reactions are involved: the reaction of lithium-6 with neutrons to produce tritons, and the reaction of these tritons with oxygen-16 to produce fluorine-18 (112 min). Because fluorine-18 decays by positron emission, detection can usually be made without further separation from other induced activities. The two 0.51-Mev gamma rays which form when the positron is annihilated are in coincidence but directionally 180° apart. For the counting of a sample, detectors are placed on either side of the sample and the circuitry is designed so that the only events registered are simultaneous 0.51 Mev pulses in each detector.

The method has also been applied to the determination of lithium in

other alkali metals. However, additional separation of the fluorine-18 from other induced activities, e.g., sodium-24 (15 hr), was necessary when the lithium concentration in the sodium was below 100 ppm. This was accomplished by adding inactive fluoride and chloride and excess lead to precipitate lead chlorofluoride. For sodium samples containing 100 ppm lithium, the relative standard deviation was 3 percent. Although no sodium metal or salts were found which contained less than 10 ppm lithium, it is estimated that the determination could be used at the one ppm level with a relative standard deviation of 10 percent.

ADDENDUM

Publications

by

Chemical Engineering Division Personnel

(From January 1, 1963 to April 30, 1964)

A. Open-Literature Publications

- Adams, M. D., D. A. Wenz and R. K. Steunenberg
Observation of a Pentavalent Uranium Species in Molten Chloride Solvents
Abstract of Papers presented at Am. Chem. Soc. Meeting, New York,
September 8-13, 1963, p. 13N
- Adams, M. D., D. A. Wenz and R. K. Steunenberg
Observation of a Uranium (V) Species in Molten Chloride Salt Solutions
J. Phys. Chem. 67, 1939 (1963) Note
- Baerns, M., F. Fetting and K. Schugerl
Investigations of Radial and Axial Gas Mixing in Fluidized Beds*
Chem. Ing. Tech. 35 (9), 609 (1963)
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Nucl. Sci. Eng. 15, 218 (1963)
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- Cafasso, F. A., H. M. Feder and D. M. Gruen
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J. Chem. Phys. 38, 1256 (1963) Letter
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Trans. Met. Soc. AIME 227, 485 (1963)

* Work performed prior to joining Argonne.

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U. S. Patent 3,119,723
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J. Phys. Chem. 67, 1506 (1963)
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Trans. Met. Soc. AIME 227, 571 (1963)
- Holmes, J. T., C. R. Wilke, and D. R. Olander
Convective Mass Transfer in a Diaphragm Diffusion Cell*
J. Phys. Chem. 67, 1469 (1963)
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- Hubbard, Ward N.
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- Irish, D. E., B. McCarroll, and T. F. Young
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* Work performed prior to joining Argonne.

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ANS Nuclear News 7(3), 3 (1964)
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Ziegler, E. N. and W. T. Brazelton
 Radial Heat Transfer in a Packed Fluidized Bed
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B. Papers Accepted for Publication in Open Literature

Baker, L., Jr., and R. C. Liimatainen
 Chemical Reactions
 Accepted for publication as a chapter of SIFTOR (Safety Information For The Technology of Reactors) to be published in two volumes by MIT Press for the AEC.

Baker, L., Jr.
 Metal-Water Reactions
 Accepted for publication as a section of Chapter 4 (Chemical Reactions) of the Oak Ridge Reactor Containment Handbook

Cafasso, F. A., H. Feder, and I. Johnson
 Partition of Solutes Between Liquid Metals. II. The Lead-Zinc System
 Accepted for publication in J. Phys. Chem.

Chandrasekharaiah, M. S.
 Dissociation Energies of Alkaline-earth Powder
 Accepted for publication in J. Phys. Chem.

Chasanov, M. G., I. Johnson, and R. V. Schablaske
 The System Zinc-Technetium-99
 Accepted for publication in the Journal of the Less-Common Metals.

Elder, J. P. and G. Wranglén
 Mass Transfer at Plane Plate Electrodes*
 Accepted for publication in Electrochemical Technology

Foster, M. S., C. E. Crouthamel, D. M. Gruen, and R. L. McBeth
 First Observation of a Solution of Li_3Bi , an Intermetallic, in Molten LiCl and LiCl-LiF
 Accepted for publication in the Journal of Physical Chemistry

Gabor, J. D.
 Lateral Solids Mixing in Fluidized-Packed Beds
 Accepted for publication in AIChE Journal

Gabor, J. D., W. J. Mecham and A. A. Jonke
 Heat Transfer in Fluidized-Packed Beds as Applied to the Fluorination of Uranium Dioxide Pellets
 Accepted for publication in the AIChE Symposium Series on Nuclear Engineering

* Work performed prior to joining Argonne.

- Levitz, N. M., J. J. Barghusen, J. T. Holmes and A. A. Jonke
 Halogenation Studies on Nuclear Fuel Element Materials in a Two-Zone
 Fluid-Bed Reactor
 Accepted for publication in the AIChE Symposium Series on Nuclear
 Engineering
- Luner, C. and M. V. Murray
 Factors Affecting the Morphology and Growth of FeSn_2 *
 Accepted for publication in J. Electrochem. Soc.
- Mecham, W. J., J. D. Gabor and A. A. Jonke
 Pilot Plant Studies of a Direct Fluorination Process Applied to Uranium
 Dioxide Reactor Fuels
 Accepted for publication in the AIChE Symposium Series on Nuclear
 Engineering
- Moriarity, J. L., I. Johnson and H. M. Feder
 The Role of Coprecipitation in Alloy Partition during the Crystallization
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 Accepted for publication in Trans. Met. Soc. AIME
- Pierce, R. D. and L. Burris, Jr.,
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