ANL-6766
General, Miscellaneous,
and Progress Reports
(TID-4500, 22nd Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1962 - April 1963

Stephen Lawroski, Division Director
R. C. Vogel, Associate Division Director
M. Levenson, Associate Division Director
V. H. Munnecke, Assistant Division Director

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

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CHEMICAL ENGINEERING DIVISION RESEARCH HIGHLIGHTS

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 reactor fuels, (2) development of methods for the synthesis and production of nuclear reactor fuels and reactor materials, (3) studies of methods for the direct conversion of heat to electricity, (4) basic engineering studies of unit operations, heat transfer, and mass transfer in nonaqueous systems, (5) basic studies of the chemistry of substances that are of interest to nuclear technology, but which are also providing data of value to the scientific community at large, (6) studies of chemical reactions that are important to the safe handling of nuclear fuels and to the safe operation of nuclear reactors, (7) determination of nuclear constants, primarily those that can be determined by chemical and radiochemical means; of particular interest are fast neutron cross sections of elements that are of importance to the design and performance of fast breeder reactors, and (8) analytical chemistry in support of the research and development programs.

I. PYROMETALLURGICAL PROCESSES

Pyrometallurgical processes are being developed for the recovery of fissionable and fertile materials from short-cooled, high-burnup reactor fuels. Such 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 molten salts are frequently used as solvents.

Lower fuel reprocessing costs are expected to result from the use of pyrometallurgical methods because they are simple, compact, and capable of handling fuel shortly after discharge from the reactor, making possible a reduction in the inventory of fuel awaiting processing. This capability for handling short-cooled fuels is a result of the stability of the process materials toward radiation. Other advantages of pyrometallurgical processes as compared with aqueous processes are direct production of solid, highly concentrated wastes, reduction of critical mass restrictions, and retention of alloying elements.

In contrast to solvent extraction and fluoride volatility processes, pyrometallurgical processes do not provide high removal of fission products. Although fission product removals are adequate to maintain satisfactory nuclear and metallurgical properties of the fuel, the residual fission product activity makes necessary remote handling during refabrication of the processed fuel. This is not considered to be a serious disadvantage for extensively recycled plutonium fuels, since even in the absence of fission products the buildup of radioactive higher plutonium isotopes would prevent direct handling of the fuel.

Because of these characteristics, pyrometallurgical processes are particularly suited to on-site processing of fast breeder reactor fuels. The processes currently under study by the Chemical Engineering Division are being developed for fast breeder reactor fuels and will be first tested in the Fuel Cycle Facility (see Section I.D) for recovery of fuel from the second Experimental Breeder Reactor (EBR-II). This integrated plant facility will be the first demonstration of a complete fuel cycle in which the irradiated fuel will be discharged from the reactor, processed and refabricated in an adjacent building, and returned to the reactor. Pyrometallurgical methods will be used for all aspects of the fuel processing.

The first core loading of EBR-II, an enriched uranium-fissium* alloy, will be recovered by melt refining, the furthest developed pyrometallurgical process at the present time. Other processes involving separations

*"Fissium" is a term which has been coined and is now widely 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.

in liquid metal and molten salt solvents are being developed for the recovery of melt refining residues, the extraction of bred plutonium from the uranium breeder blanket, and the processing of future core loadings which will contain plutonium.

A. Melt Refining Process

The first core loading of EBR-II consists of approximately 50 percent enriched uranium alloyed with five percent fission. The fuel elements consist of individual fuel pins, 0.144 inch in diameter and about 14 inches long, clad with 10-mil stainless steel jackets which are thermally bonded to the fuel by sodium in the annulus. In preparation for processing partially spent fuel by melt refining, the fuel pins are declad mechanically and chopped to a convenient length (about two inches) for handling.

The melt refining process consists of charging about 10 kg of the chopped pins to a lime-stabilized zirconia crucible, melting, and liquating the molten metal at 1400 C under an argon atmosphere for about three hours. Induction heating is used, and the crucible is covered by a Fiberfrax* fume trap to collect volatilized sodium and fission products. The equipment is enclosed by a steel bell jar to permit the use of vacuum and a high-purity inert atmosphere. During melt refining, approximately two-thirds of the fission product elements are removed through the mechanisms of volatilization and reaction with the oxide crucible. Most of the volatilized fission products other than krypton and xenon are condensed on the Fiberfrax fume trap. The purified metal is recovered by top-pouring into a mold. The oxidized fission products remain in the crucible as a skull composed mainly of oxidized and unpoured uranium metal. An auxiliary process utilizing liquid metal solvents (see Skull Reclamation Process) is employed to reclaim the skull material, which ordinarily amounts to about ten percent of the original melt refining charge.

The development work on the melt refining process is essentially completed, and plant equipment has been installed in the EBR-II Fuel Cycle Facility. During the year, additional work has been devoted to (1) a fifth and final laboratory-scale experiment in which about 0.4 kg of highly irradiated fuel was melt refined, (2) the behavior of fission product iodine released during melt refining, (3) the possible use of molten halide fluxes in the melt refining process, (4) the nitridation of irradiated fuel in argon-nitrogen atmospheres, and (5) methods for the removal of nitrogen from argon.

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

1. Melt Refining Demonstration Runs with Highly Irradiated Fuel Alloy

The last of a series of five demonstration experiments using highly irradiated EBR-II prototype fuel alloy has been completed. The fuel, composed of ten percent enriched uranium alloyed with five percent fission, was irradiated to a burnup of 1.75 total atom percent. The total beta and gamma activity of the 382-gram charge used in the experiment was about 4700 curies. The charge was melt refined under argon for one hour at 1400 C. The fission product removals (see Table I-1) were virtually identical to those obtained in the other four experiments in which the burnups varied from 0.22 to 0.87 total atom percent. Consideration of all the results obtained in these studies indicated that burnup, radiation level, or the duration of melt refining (1 and 3 hours) had no significant effect on the extent of fission product removal. As shown in Table I-1, the rare earths, yttrium, tellurium, iodine, cesium, barium, and strontium were removed. As was expected, the noble metals, ruthenium and molybdenum, were not removed. Some fission product zirconium underwent isotopic exchange with inactive zirconium from the zirconia crucible. However, a slight removal of zirconium occurred, probably by reaction of the zirconium with carbon contaminants.

Table I-1

FISSION PRODUCT REMOVALS DURING FIVE MELT
REFINING EXPERIMENTS USING HIGHLY
IRRADIATED FUEL ALLOY

<u>Fission Product Element</u>	<u>Percent Removal</u>
Rare Earths and Yttrium	97-99+
Tellurium	95-99+
Zirconium	9-28
Iodine	99+
Cesium	99+
Barium and Strontium	99+
Ruthenium	0
Molybdenum	0

A surface slag layer formed in the runs with irradiated material and caused somewhat lower pouring yields. The lower pouring yields may have resulted from the oxidation that occurred during handling of self-heated, irradiation-roughened pins in an air atmosphere. This is unlikely to occur in plant operation, in which the pins will be handled in an inert argon atmosphere.

Observations of the physical characteristics of the irradiated fuel alloy showed it to be very brittle and easily shattered under compressive stress in a vise or under a sharp impact. The gross swelling which is characteristic of the irradiated alloy upon heating through the temperature interval of about 650 to 900 C caused no difficulties in the small-scale melt refining experiments.

2. Fate of the Iodine-131 in Melt Refining

Because of its radiobiological properties, fission product iodine-131 which is released in the melt refining process requires special provisions* to prevent its release to the atmosphere in excessive concentrations. Therefore, information pertinent to the handling of radioiodine was obtained during the course of the melt refining studies with highly irradiated fuel and in separate laboratory experiments in which 7-gram pieces of the irradiated uranium-fissium fuel pins were melted and held at 1400 C. In the latter experiments, the only fission products collected on a tantalum condenser above the melt refining crucible were cesium and iodine. No appreciable volatilization of uranium, noble metals, tellurium, alkaline earths, or rare earths was detected. The overall material balances for iodine in these experiments were low (30 to 50 percent), and additional studies are underway to determine the cause of these low values. Nevertheless, some pertinent information was obtained on the iodine distribution during melt refining. It was found that most of the iodine had volatilized and had deposited on regions of the tantalum condenser which had been in the temperature range of 450 to 700 C during the experiment. This relatively high condensation temperature suggests that the iodine was collected in the form of a compound, rather than as the element. It is believed that the compound was cesium iodide (m.p. 621 C; b.p. 1280 C), since fission product cesium was also found in this portion of the condenser in amounts exceeding the stoichiometric requirement for cesium iodide. The atmosphere (argon) was found to contain about 0.005 percent of the original iodine, the product ingot about 0.1 percent, and the skull (or melt refining residue) about 1.2 percent before it was oxidized. After the skull was oxidized, it contained about 0.25 percent of the iodine in the original melt refining charge, indicating that provisions are necessary for handling iodine activity in the off-gases from the skull oxidation equipment.

In the high-activity-level melt refining experiments an off-gas handling system was used that was functionally similar to that being provided in the EBR-II Fuel Cycle Facility, in order to evaluate the performance of various components. The iodine-removal equipment consisted of two high-efficiency AEC filters separated by a seven-section charcoal trap.

*Charcoal traps, high-efficiency filters, and a holding tank are being provided in the appropriate off-gas line of the EBR-II Fuel Cycle Facility.

At the conclusion of Melt Refining Run No. 5, only about 1.5×10^{-3} percent of the iodine activity originally present in the melt refining charge was found in the argon atmosphere of the furnace. This atmosphere was pumped from the furnace through the charcoal trap assembly. Table I-2 shows the distribution of the iodine-131 activity collected on the various components of the trap assembly. The effluent argon from the assembly contained an insignificant amount of iodine-131 activity i.e., less than 6×10^{-6} percent of that originally present in the melt refining charge.

Table I-2

IODINE-131 DISTRIBUTION ON AEC FILTER-CHARCOAL
TRAP ASSEMBLY USED IN HIGH-ACTIVITY-LEVEL
MELT REFINING EXPERIMENT NO. 5

The total iodine activity in the melt refining charge was
 1.7×10^7 microcuries.

Component	Iodine-131 Activity (microcuries)
Inlet AEC Filter	182
Charcoal-First Section	68
Charcoal-Second through Seventh Sections	$<10^{-4}$
Outlet AEC Filter	6.2×10^{-2}

3. Possible Use of Salt Fluxes in Melt Refining

The use of salt fluxes to remove fission products from molten metallic fuel in an inert crucible constitutes a possible improvement in the melt refining process. The potential advantages are increased yields, more efficient fission product separations, and the reuse of crucibles. Molten oxide fluxes were considered briefly, but were rejected because they attack standard crucible materials, such as beryllia, alumina, and zirconia. Encouraging results were obtained, however, with calcium chloride fluxes containing a small amount (5 to 10 weight percent) of a mild oxidizing agent, for example, magnesium fluoride. These fluxes have satisfactorily low melting points (~ 800 C), and can be contained in beryllia crucibles. Several 700-gram charges of uranium-5 percent fission alloy containing between 0.5 and 0.8 weight percent cerium were melt refined in beryllia crucibles, using a liquation time of one hour at 1100 to 1300 C and a calcium chloride flux containing magnesium fluoride to oxidize the more electropositive fission products. Pouring yields above 97 percent of metallic uranium charged were obtained, compared to about 88 percent for melt refining in zirconia crucibles in the absence of a flux under similar conditions of temperature and time. Cesium and cerium removals were approximately 99 and 97 percent, respectively. Uranium losses to the flux were

0.03 percent or less, and there was no evidence of crucible attack. A literature survey on similar systems indicates that plutonium losses by volatilization and extraction into the flux should not exceed one percent. Some additional experimental work is planned to check plutonium behavior in this process.

4. Nitridation Rates of Uranium-Fissium Alloys

At present, no method is provided for nitrogen removal from the Argon Cell of the EBR-II Fuel Cycle Facility at Idaho other than purging provided by the normal additions of pure argon during operation, although the equilibrium nitrogen concentration resulting from inleakage of air may be as high as five percent.* Further studies have therefore been made of the nitridation rates of irradiated uranium-fissium alloys in argon-nitrogen atmospheres. The measurements were made at various temperatures, since fission product decay heat will raise the temperature of the irradiated fuel. At 300 C, with burnups of zero to 1.18 total atom percent and specific activities up to 14.3 curies per gram, the effect of irradiation on the nitridation rate in 100 percent nitrogen was small (see Figure I-1). At temperatures above about 650 C, however, nitridation became rapid and self-sustaining, as indicated by the heating curves shown in Figure I-2. This behavior occurred only at nitrogen concentrations above 0.5 percent. Swelling and rapid release of the fission product gases krypton and xenon occur in this temperature region, and it is believed that the increase of surface area resulting from these effects is related to the rapid nitridation rates observed.

Further work also was done in an investigation to determine the effect of prior nitridation of the fuel on melt refining yields. Approximately two-kilogram charges of unirradiated uranium-fissium fuel pins, containing about 0.5 percent cerium to simulate rare earth fission products, were first stored for two hours at 350 or 650 C in argon atmospheres containing nitrogen, and were then melt refined for three hours at 1400 C. The results are shown in Table I-3. The extent of nitridation during storage was in good agreement with the earlier laboratory data on nitridation rates. In all instances, prior storage of the fuel pins in the nitrogen-containing atmospheres had a negligible effect on the melt refining yield. This result is also in agreement with earlier studies. Apparently, as long as the irradiated fuel in the Argon Cell is not allowed to exceed a temperature of about 600 C, nitridation will not be sufficient to interfere with the melt refining process. Precautions are required, however, to avoid exceeding about 650 C, where rapid nitridation appears to occur in association with swelling of the fuel.

*Provisions have been made to remove water vapor and oxygen from the argon atmosphere of the Argon Cell in the EBR-II Fuel Cycle Facility at Idaho. The resulting equilibrium levels are expected to be about 5 and 20 ppm, respectively. Removal of nitrogen from argon with titanium sponge is being studied, and is discussed in a following section.

Figure I-1

NITRIDATION RATES OF IRRADIATED FISSIUM III ALLOY

Atmosphere: nitrogen, 1 atm

Temperature: 300 C

Alloy: Fissium III (irradiated in MTR as indicated): Fissium II: 94.4 w/o natural uranium,
 85 w/o U^{238} , 10 w/o U^{235} , 2.5 w/o Mo, 2.5 w/o Mo, 1.9 w/o Ru, 0.3 w/o Rh,
 1.9 w/o Ru, 0.3 w/o Rh, 0.2 w/o Pd, 0.2 w/o Pd, 0.1 w/o Zr, 0.6 w/o Ce.
 0.1 w/o Zr

Curve	Material	Burnup (atom percent)	Cooling Time (days)	Specific Activity (c/g)	Prior Air Exposure (hr)	NaK Removal Method
1	Fissium III	1.18	20	14.3	<1	oxidation
2	Fissium III	0.87	100	4.3	<1	oxidation
3	Fissium III	0.74	240	1.26	<1	1-butanol
4	Fissium II	0	-	0	<1	-

Figure I-2

TIME-TEMPERATURE CURVES FOR IRRADIATED FISSIUM III IN NITROGEN-ARGON MIXTURES

Conditions

Number of Pins: 1
 Burnup (total atom percent): 1.18
 NaK Removal Method: oxidation
 Cooling Time (days): 100
 Flow Rate (cc/min): 100
 Heating Rate (C/min): ~10

Fissium III composition

85 w/o U^{238} , 10 w/o U^{235} , 2.5 w/o Mo,
 1.9 w/o Ru, 0.3 w/o Rh, 0.2 w/o Pd,
 0.1 w/o Zr.

Table I-3

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

Storage Conditions

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

Melt Refining Conditions

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

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

^aAverage of two runs from previous series.

5. Removal of Nitrogen from Argon with Titanium Sponge

Because there is the possibility that for other fuel materials and other fuel recovery processes, removal of nitrogen from the Argon Cell atmosphere will be required, a project has been initiated to investigate the removal of nitrogen from argon by gettering the nitrogen with titanium sponge. Titanium sponge was chosen as the gettering material because of its high efficiency and low cost per mole of nitrogen-removal capacity. The present study is being carried out in two parts: (1) the study of the kinetics of the titanium-nitrogen reaction and (2) construction and operation of a scale model of the proposed plant system. The main objectives of the latter study will be to test equipment designs, to obtain data on equipment reliability, and to obtain operating experience.

A preliminary study of reaction kinetics has been made at 900 C using a thermobalance. Results have indicated that solid-state diffusion of nitrogen in titanium strongly influences reaction kinetics. Because of the resulting sensitivity of reaction rate to the nitrogen gradient existing in the solid phase, accurate reaction rates over a titanium conversion range of 0 to 50 percent can be established only by long operation with a feed gas containing a low partial pressure of nitrogen.

This requirement is being fulfilled in new equipment which is under construction. In this equipment, an argon-nitrogen mixture of carefully controlled composition (50 to 5000 ppm of nitrogen) will be continuously circulated through a series of small titanium beds. The circulating rate will be such that only a small fraction of the nitrogen in the gas will react in a single pass. The entire nitrogen content of the gas will be removed in each pass by a large titanium bed and then will be replaced by a slow bleed of nitrogen into the system just in front of the titanium test beds. The nitrogen concentration will be controlled by careful regulation of the flow rates of the argon and nitrogen streams. The extent of reaction of the titanium test material will be determined at intervals by removing the first titanium bed in the series and analyzing it for nitrogen. The bed will not be replaced, nor will succeeding beds as they are successively removed. Therefore, the number of values obtained will be equal to the number of test beds initially used. The rate of reaction for a particular titanium conversion will be determined by differentiation of the curve which gives the relationship between the extent of reaction and time. Assembly of the equipment for this study is nearly complete, and experimental work will be started soon.

In the pilot plant system now under design, argon will be circulated through the purification equipment at a rate of 10 cfm. Pure nitrogen will be bled into the loop to produce the desired nitrogen concentrations. Removal of the nitrogen will be accomplished in a bed containing approximately 30 pounds of titanium sponge and operating at 900 C. Regenerative heat exchangers will be employed to cool the exit gases and preheat entering gases. It is expected that this unit will become operational in the third quarter of 1963.

B. Processes Employing Liquid Metal Solvents

Several liquid metal processes are being developed for the recovery of spent reactor fuels and for the synthesis or preparation of reactor fuel materials. The skull reclamation process for recovering the fissionable material remaining in the crucible residue (skull)* after a melt refining operation has been investigated further in small-scale demonstration runs. Equipment development studies and larger scale demonstration experiments are also now being conducted in essentially full-scale integrated process equipment. Demonstrations of a liquid metal process for the extraction of plutonium from EBR-II blanket material have continued. Laboratory development work is also continuing on processes for preparing other fuel materials, especially those which will contain plutonium as a fissionable material.

Supporting fundamental studies of liquid metals and molten salts of process interest are in progress. These studies include the chemistry involved in process steps and the accumulation of information of engineering importance, such as data on distillation, heat transfer, mass transfer, and mixing characteristics of liquid metals and salts.

1. Skull Reclamation Process

The skull reclamation process is being developed as an auxiliary to the melt refining process of the EBR-II fuel cycle. After a melt refining operation, about ten percent of the fuel remains in the melt refining crucible as a "skull" (a mixture of oxides and unpoured metal adhering to the crucible walls). The major objective of the skull reclamation process is the recovery of fissionable material from the melt refining residues. The process must also effect purification of the reclaimed fissionable material from fission products. Fission products include the relatively noble elements that are not removed in melt refining (zirconium, molybdenum, technetium, ruthenium, and palladium), and the rare earth and alkaline earth fission product elements that are removed from the bulk fuel material in melt refining by concentrating them in the skull material.

The major features of the skull reclamation process have been established for some time. The process flowsheet is presented in Figure I-3. The process consists of (1) an oxidation step that converts the skull material to free-flowing oxides which are poured from the zirconia melt refining crucible, (2) selective extraction of the noble fission products

*Skull material (after the first cycle in the EBR-II reactor) is expected to have the following approximate composition: 6 percent rare earths, 2 percent molybdenum, 1.5 percent ruthenium, 0.2 percent palladium, 0.3 percent rhodium, 0.4 percent zirconium, traces of other fission product elements, and the balance uranium.

into molten zinc from a slurry of the oxides in a halide flux, (3) reduction of the uranium oxides by and dissolution of the uranium in a magnesium-zinc solution, (4) two uranium precipitations (first as a uranium-zinc intermetallic compound and then as uranium metal) designed to concentrate the uranium and also to purify it by removal of impurities in the supernatant metal solutions, and (5) a retorting step for removal of residual metal solvents from the uranium products.

Figure I-3

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

U PRODUCT

Work during the past year has been concentrated in the following areas:

- 1) small-scale demonstrations of the skull reclamation process for the purpose of pinpointing and solving process problems,
- 2) development of engineering procedures,
- 3) design and construction of an engineering-scale pilot plant (about one-half plant scale, i.e., 2 kg of uranium) for large-scale demonstrations of equipment and process performance, and
- 4) testing of potential materials of construction.

Following this work, the process and equipment must be demonstrated under remote operating conditions before the process will be ready for installation in the EBR-II Fuel Cycle Facility.

a. Small-Scale Demonstrations of the Skull Reclamation Process

Small-scale demonstrations of the skull reclamation process (100 to 150 grams of uranium) were made in equipment located inside an argon-atmosphere glove box in order to simulate conditions in the argon-atmosphere processing cell of the Fuel Cycle Facility. The skull oxide charges were prepared from unirradiated uranium-fissium skulls which contained cerium as a stand-in for all rare earth elements. Two problems, poor removal of ruthenium in the noble metal extraction step and inadequate removal of zirconium when a large quantity of zirconia crucible fragments is present, were revealed by the demonstration runs and were made the subjects of special studies.

The problem of poor ruthenium removal in the noble metal extraction step* was noted when demonstration runs were first made in the inert atmosphere glove box. Ruthenium removals of less than 10 percent were obtained, as compared with 70 percent or greater in previous runs. Previous runs had been conducted in closed equipment containing argon, but with charges which had been exposed briefly to air. In glove box runs, all operations including charging were done in an inert atmosphere and the poor extraction of ruthenium was attributed to a lack of oxidizing power resulting from the elimination of water. This hypothesis appeared to be confirmed when good ruthenium removals (near 100 percent) were achieved in runs in the inert atmosphere glove box by the addition of a small quantity of water or zinc chloride oxidant to the flux phase in the noble metal extraction step. However, in the runs in which good ruthenium extraction was obtained, less than the normal amount of zinc was used in order to increase the concentration of ruthenium in the zinc extract and thereby effect an improvement in the accuracy of ruthenium analyses. The resultant change in zinc volume moved the flux-metal interface from a location several inches above the agitator to a location near the agitator. This change in mixing conditions may have contributed to the improvement in ruthenium extraction, and the effect of this change is currently being determined.

*In the noble metal extraction step, which follows oxidation of the crucible skull material and removal of the oxidized skull from a melt refining crucible, the skull oxides are suspended in a chloride flux (composition in weight percent: 47.5 magnesium chloride, 47.5 calcium chloride, and 5 magnesium fluoride), and this flux-oxide suspension is vigorously contacted with molten zinc at 800 C in order to leach or extract from the flux the noble metal fission products.

Sufficient zinc chloride (concentrations up to 10 percent) will be employed as a standard constituent in the flux phase in the noble metal extraction step to oxidize into the flux phase any metallic uranium that might be present, such as, for example, any unoxidized uranium in the skull oxide. Thereby, loss of uranium in the waste zinc phase will be prevented.

By use of zinc chloride, the skull reclamation process may be able to accommodate damaged or non-decladdable fuel pins, or scrap uranium from other parts of the fuel cycle. Stainless steel cladding is quickly dissolved or corroded by zinc at 800 C. Experiments have shown that after oxidation of the uranium into the flux in the noble metal extraction step, iron and nickel remain essentially completely in the zinc phase. However, a substantial extraction of chromium along with uranium into the flux phase occurs, and a means of separating chromium from uranium must be provided. The chromium distribution coefficient of 0.36 (weight percent in flux/weight percent in metal) is such that a second contact of the flux with zinc would provide adequate chromium removal if the distribution coefficient remained at the above value. This is now being investigated.

Zirconium is introduced into the skull reclamation process from two sources: (1) the fuel material itself, i.e., through the fission process (which results in the introduction of 0.25 weight percent zirconium for a fuel burnup of 2 percent) and (2) fragments or particles of the zirconia crucible which may slough off into the skull oxide. Since it was believed that the only mechanism for zirconium removal was its removal in the supernatant waste metal solution of the zinc-uranium intermetallic compound precipitation step, it became necessary to determine the maximum zirconium-removal capability of the process.

Since zirconium does not coprecipitate with the uranium-zinc intermetallic compound (ANL-5294, page 136), the maximum amount of zirconium which can be removed in the zinc-5 weight percent magnesium supernatant solution is determined by the solubility of zirconium in the supernatant solution. The solubility of zirconium in this supernatant solution was found to be 0.11 percent at 500 C and 0.20 percent at 525 C. Because uranium loss (as a result of uranium solubility in the supernatant solution) becomes excessive at temperatures above 525 C, this latter temperature is the maximum practical temperature of operation. The zirconium solubility of 0.2 percent and the weight of supernatant solution are such that with the expected 85 percent removal of the supernatant solution satisfactory zirconium removal can be achieved with skull oxide containing up to about two percent zirconium. This is more than adequate for the removal of zirconium whose source is the fuel material itself, which will contain well under 1 percent zirconium. Generally, the concentration of crucible fragments in skull oxides is about one percent, and results in a total zirconium

concentration that can be readily accommodated in the process. However, concentrations of crucible fragments of up to 3 percent may be occasionally encountered. This is not of real concern since occasional high concentrations of zirconium in the fuel will not impair the performance of the fuel, and since the zirconium concentration will be lowered in the course of future processing cycles.

Satisfactory removal of fission products was demonstrated in two runs (see Table I-4), although the ruthenium removal in Run BJ-16 is the minimum which can be regarded as satisfactory. The relatively low ruthenium removal in Run BJ-16 resulted from the deliberate omission of stirring of the zinc extract before and during transfer of the zinc to determine if the noble metals would remain in suspension without stirring. The low ruthenium removal indicates that stirring will be necessary. The removals in these runs confirm those of previous runs. Uranium recoveries of about 95 percent were realized in these runs. These recoveries are adequate, since only about 10 percent of the total fuel is processed through the skull reclamation process, but better recoveries are anticipated in larger-scale runs.

Table I-4
PERFORMANCE OF SKULL RECLAMATION PROCESS IN TWO SMALL-SCALE DEMONSTRATION RUNS
(BJ-16 and BJ-17)

Constituent	Charge Composition, Oxygen-free Basis (w/o)	Run BJ-16			Run BJ-17		
		Uranium Yield (%)	Fission Product Removal (%)	Prod. Comp. (w/o)	Uranium Yield (%)	Fission Prod. Removal (%)	Prod. Comp. (w/o)
Uranium	77	95 ^a	-	94.9	95	-	94.5
Cerium ^b	5.9	-	96	0.37	-	92	0.63
Molybdenum	2.0	-	80	0.60	-	72	0.74
Ruthenium ^c	1.6	-	55	1.1	-	93	0.15
Zirconium	13.3	-	85	3.0	-	87	3.9

^aIncludes uranium in reduction heel and on agitator shaft which is normally recycled.

^bCerium was present in the skull oxide as a stand-in for all rare earth elements.

^cPalladium and rhodium are minor constituents of fission. Their removals are considerably better than that of ruthenium. The low value of ruthenium removal in Run BJ-16 resulted from the deliberate omission of stirring in the noble metal extraction step.

Summary

The work described above shows the following:

- 1) The skull reclamation process, which is complementary to the melt refining process in the EBR-II fuel cycle, is capable of providing adequate uranium recovery (at least 95 percent).
- 2) Adequate purification can be achieved from all fission product elements with the possible exception of zirconium.

- 3) A capability for adequate zirconium removal exists when the concentration of zirconia crucible fragments in the skull oxide does not exceed about two to three percent. This latter value is expected to occur only rarely and is considered an abnormally high concentration; nevertheless, this process limitation should be recognized.

b. Development of Engineering Procedures

The major engineering procedures required in the skull reclamation process are: (1) materials handling, (2) mixing of metal and flux phases, (3) separation and transfer of flux and metal phases, and (4) retorting of the uranium product. Although all of these areas have received some attention, the major effort to date has been given to the development of phase separation procedures and equipment and to the study of the retorting operation.

Mixing

Mixing of metal and flux phases, separately and together, has been satisfactorily accomplished by conventional mechanical mixers operating in vertically baffled vessels. A dynamometer was constructed for measuring mixing power inputs to metal and metal-flux process systems. It was found that the mixing power input into mercury can be represented by the same correlations previously developed for aqueous and organic systems. Inductive mixing is currently being investigated as an alternative procedure because it may be more suitable for remote operation than mechanical mixing.

Phase Separations

The method which has been adopted for the separation and transfer of liquid phases is called pressure-siphoning. It consists essentially of applying gas pressure to the top surface of a liquid in one container and thereby transferring the liquid through a pipe from one vessel to another vessel or to a waste container. In this manner, 90 to 95 percent of the zinc extract of the noble metal extraction step is transferred from beneath a solidified flux to a waste container.

For effecting an essentially automatic separation of flux and metal phases at 800 C after reduction of uranium oxides, a system of two transfer tubes has been developed. Highly satisfactory separation of the molten phases (each approximately one liter in volume) has been repeatedly demonstrated at practical transfer rates. However, because malfunction of this system would not be detected and would result in transfer

of the two phases together, which is highly undesirable, an alternative procedure has been developed by which the phases may be sequentially transferred by manually controlled pressure siphoning, using a bubbler gauge to determine the level of the interface.

The transfer of the supernatant solution from a precipitated uranium-zinc intermetallic phase was studied some time ago. Eighty to ninety percent removals of the supernatant were achieved without difficulty.

Removal of the 50 percent magnesium-zinc solution from precipitated uranium metal is a phase separation common to both the blanket and skull reclamation processes. In ten runs made on a 5-kg uranium scale, supernatant removals ranged between 93.5 and 97.5 percent. Uranium entrainment was negligible in most of these runs.

Retorting

The vaporization (i.e., retorting) of residual magnesium and zinc from the uranium product of the skull reclamation process can be carried out above 700 C at whatever pressure and corresponding temperature appears practical. For plant operation, atmospheric pressure may be the most convenient. It is considered desirable to consolidate the uranium product by melting it at the conclusion of the retorting operation.

The selection of a container material has been given principal attention in the past year. It is of prime importance that the material chosen release the uranium product obtained in the skull reclamation process. Metals are unsatisfactory. Of the ceramics, beryllia is the most suitable because it is not highly susceptible to thermal shock and is not wet by the metal systems.

Large-size beryllia crucibles have hitherto been unavailable. Discussions of this problem with manufacturers of beryllia led to a suggestion by the Brush Beryllium Company that thixotropic casting might be a feasible procedure for manufacture of large beryllia crucibles. Initial testing was carried out with small-size thixotropically cast beryllia crucibles (4 in. OD by 9 in. high) to assess their performance in the precipitation and retorting steps. The performance of these crucibles was very good. One crucible was subjected to process conditions simulating 24 intermetallic precipitation steps, 25 intermetallic decomposition steps, and 10 final retorting steps before it was judged to be too unsound for further use. During the precipitation steps of these runs, the crucible successfully contained zinc-magnesium solutions at temperatures above 450 C for about 465 hours. For comparison, approximately 20 hours is estimated to be the time that a crucible will be exposed to similar conditions in processing a single batch of material on a plant scale. Essentially 100 percent of the

isolated uranium product was easily recovered from the crucible after each of the ten retorting steps. As indicated in the following section of this report, large size beryllia crucibles made by thixotropic casting have now been procured for use in the large-scale equipment for the skull reclamation process.

c. Large-Scale Integrated Equipment for the Skull Reclamation Process

Construction of the integrated equipment for large-scale (2 kg of uranium) demonstrations of the skull reclamation process has been completed, and equipment shakedown testing has begun. The equipment consists of two large, normally stationary, easily replaceable crucibles which are positioned centrally within metal bell jars. One of these crucibles, a 500-lb pressed-and-sintered tungsten crucible (12 in. OD by 19 in. high) serves for the first two steps of the skull reclamation process; the other, a thixotropically cast beryllia crucible of about the same size ($11\frac{1}{2}$ -in. OD by 20 in. high), serves for the two precipitation steps which follow. The uranium concentrate (uranium enveloped in a 50 percent magnesium-zinc alloy) obtained in the second precipitation step will be removed and retorted in another beryllia crucible.

The metal bell jars are about 30 in. in diameter and 40 in. high and can be tightly closed for containment of a high-purity argon atmosphere. Heating will be effected by means of graphite susceptors heated by radiant-cooled copper induction coils. As indicated previously, solution removal for the necessary phase separations will be effected by pressuring the liquid out through dip tubes (pressure-siphoning).

Figure I-4(a) is a photograph of the integrated equipment showing the bell-jar covers in place. A transfer line is shown in position for transfer of molten metal from one furnace to the other. Other important features of the equipment are indicated in Figure I-4(b). In Figure I-5, the bell jar cover has been removed from each furnace, showing a large pressed-and-sintered new tungsten crucible in position within one induction heating coil and a similar large beryllia crucible in the other.

Ultimately, this equipment will be enclosed in a glovebox, the frame of which is shown in Figure I-6, for operation in an inert argon atmosphere. Preliminary process operations in air have been started in order to facilitate any necessary equipment corrections or changes in operating procedures. Various operating characteristics have been determined in these starting operations, e.g., required power inputs, heating and cooling rates, and equilibrium temperatures of the induction coils. All phase transfers and separations have been satisfactorily made.

Figure I-4
LARGE-SCALE INTEGRATED EQUIPMENT FOR THE
SKULL RECLAMATION PROCESS

(a) Two furnaces installed in glovebox frame

(b) Two furnaces and two waste containers

Figure I-5

SKULL RECLAMATION FURNACES WITH BELL JARS REMOVED

A once-used beryllia crucible, a graphite susceptor, a Fiberfrax insulator, and induction heating coil are shown.

A new tungsten crucible, graphite susceptor, Fiberfrax insulator and induction heating coil are shown.

After several equipment changes have been made, full-scale process runs will be started. This pilot plant will probably be operated throughout 1963. However, design of mockup equipment may begin earlier if no difficulties are encountered in test runs.

d. Materials of Construction

Only tungsten and certain tungsten alloys and stable ceramic materials (such as beryllia and possibly alumina) possess adequate resistance to corrosion by the zinc and molten salt systems of the skull reclamation process. Virtually no corrosion of tungsten by the zinc-molten salt system used in the noble metal extraction step has been found (see Table I-5). Probably as a result of annealing, the mechanical properties of tungsten (as represented by the modulus of rupture) were improved considerably over the corrosion test period. In other work, medium-size, pressed-and-sintered tungsten crucibles (4 in. OD by 9 in. high) have not been visibly affected by over 1000 hours of exposure to process solutions of the noble metal extraction and reduction steps.

Figure I-6

FURNACES, GLOVEBOX FRAME, AND PANEL-
BOARD FOR SKULL RECLAMATION PROCESS
DEMONSTRATION

Table I-5

CORROSION OF TUNGSTEN AND TUNGSTEN ALLOY COUPONS BY THE
SALT-METAL^a SYSTEM OF THE SKULL RECLAMATION PROCESS

Temp 800 C
Time 500 hours
Agitation 460 rpm

Material	Weight Change (%)	Depth of Attack (mils)	Avg Modulus of Rupture (psi)	
			Before Exposure	After Exposure
Pressed and Sintered Tungsten	-0.2 to +0.1	1	50,000	65,000
Sintered and Rolled Tungsten Sheet	-0.02	1	110,000	145,000
70% Mo-30% W Alloy	-3.8	4 to 8	210,000 ^b	175,000 ^b

^aThe salt phase weight was 425 g; its composition was 46.6 m/o LiCl, 46.6 m/o MgCl₂, 4.8 m/o MgF₂ and 2.0 m/o ZnCl₂. The zinc metal phase weighed 1350 g. This is the system used in the noble metal extraction step.

^bThese values should be compared with each other only since the formula does not strictly apply to this alloy because of plastic deformation of the sample.

Tungsten, however, is not readily fabricable into relatively complex shapes, such as transfer piping and agitators. For these components, a machinable molybdenum-30 percent tungsten alloy has been found to be satisfactory. Corrosion resistance of this alloy to process systems is not as good as that of pure tungsten (see Table I-5) because of slow leaching of molybdenum, but is sufficiently good to allow several thousand hours of process use of the easily replaceable items fabricated from this alloy.

As pointed out previously in the discussion of retorting, a ceramic crucible material is desirable for the last three steps of the skull reclamation process to allow ready release of the uranium product. Beryllia is presently judged to be the most suitable material for these steps, but other ceramics are being tested and developed. Anodized beryllium (that is, beryllium metal coated with beryllium oxide by an anodization process) has also been considered for the precipitation and retorting steps of the skull reclamation process because beryllium metal possesses greater strength and density than does beryllia. However, the anodized coating proved to be nonadherent and did not protect the beryllium from attack by zinc-magnesium and halide flux systems.

The adequacy of stainless steel for housing the container vessels used in experimental work with zinc systems was also investigated. (A housing is needed when it is desired to maintain an inert atmosphere and operate at desired pressures.) It has often been observed that stainless steel (usually Type 304) suffers little attack by zinc vapor but is severely attacked by liquid zinc in areas where condensation of zinc occurs. Because stainless steel may be considered for applications in which it would be exposed to attack by zinc vapor only, the extent of attack of several stainless steels by zinc vapor was determined. In 500-hour exposure to zinc vapor at 900 C, two austenitic 300 series stainless steels (Types 304 and 347) suffered severe attack. Loss of nickel from these steels indicates the probable formation of low melting phases. Good corrosion resistance to attack by zinc vapor was exhibited by a 400 series stainless steel, Type 405, a ferritic steel. Another 400 series stainless steel, Type 440 C, a martensitic steel, also exhibited fairly good corrosion resistance, although suffering some loss in weight.

2. Blanket Process

The objective of the blanket process for discharged EBR-II blanket material is to increase the concentration of plutonium in discharged blanket material from an initial 1 weight percent in uranium to a value of at least 40 percent so that it may be used for enrichment of core materials. The blanket process flowsheet is shown in Figure I-7. Sufficient blanket material is first dissolved to give a concentration of about 14 weight percent uranium in a 12 weight percent magnesium-zinc alloy. Uranium is then precipitated by adding sufficient

magnesium so that the magnesium concentration is 50 weight percent. The plutonium is in the supernatant solution, which is separated from the uranium precipitate and boiled down to give a plutonium concentrate suitable for feeding into the core cycle.

Figure I-7

EBR-II LIQUID-METAL PROCESS FOR URANIUM BLANKET METAL

Two additional blanket process demonstration runs, which were carried to the point of solution boil-down, are summarized along with previously reported runs in Table I-6. All were characterized by rapid dissolution of the uranium, good material balances for plutonium and uranium, and good separation of plutonium from uranium. Table I-6 lists the separation factors, defined as plutonium-to-uranium ratio in the product divided by the same ratio in the feed material. Separation factor values varied from about 160 (a 62 percent plutonium-uranium product) to about 230 (a 70 percent plutonium-uranium product). A separation factor of 240 is about the maximum that could be realized in the plutonium product supernatant solution. The low separation factor in Run 4 is the result of an unusually high physical carryover of uranium in the magnesium wash solution.

Table I-6

SUMMARY OF BLANKET PROCESS DEMONSTRATION RUNS

Scale of Operation: 500 g of 1 percent Pu-U Alloy

Run No.	Pu Recovery (%)	Pu/(Pu + U) in Product	Separation Factor ^a
1	92	0.65	168
2	95	0.65	169
3	93	0.61	157
4	100	0.44	77.5
5	92	0.70	230

^aSeparation factor is defined as the plutonium-to-uranium ratio in the product divided by the plutonium-to-uranium ratio in the feed material. In all runs except Run 5, the uranium precipitate was washed with 2 kg of 50 weight percent magnesium-zinc alloy. The use of a wash, while increasing the percentage of plutonium recovered, reduces the separation factor since additional uranium is dissolved in the wash solution. The separation factor of 230 realized in Run 5 is near the maximum achievable in this process.

The above plutonium product concentrations (which would be achieved by boiling off the zinc and magnesium solvents) substantially exceed the process requirement, since a minimum of 40 percent plutonium in plutonium-uranium alloy will be used for re-enrichment of an EBR-II core. Moreover, during boildown of the product solution, additional uranium will precipitate and be separable from plutonium, thus providing a considerable increase in the plutonium-uranium separation factors. No effort will be made to remove this uranium until sufficient buildup has occurred to warrant a removal operation after dissolving it in zinc.

Analyses for plutonium content were made at each step of the blanket runs. Plutonium recovery was found to be the same (within analytical accuracy) as the percentage removal of the supernatant product phase. Phase separations achieved in the small-scale runs have been such that phase separation efficiencies of at least 95 percent are expected on a plant scale. Such efficiencies were, in fact, consistently demonstrated in a separate series of runs on a 5-kilogram scale using uranium alone. If higher plutonium recoveries are desired, the uranium precipitate may be washed with the 50 percent magnesium-zinc alloy as in Run 4, Table I-6. Any unrecovered plutonium remains with the uranium precipitate, which will be either discarded or recycled back to the reactor blanket.

In order to obtain information on fission product behavior in the blanket process, one demonstration run was made with a lightly irradiated uranium charge. Plutonium was left out of the charge in order to facilitate fission product analyses. Although in actual operation the blanket material may be cooled for a considerable time before processing, allowing decay of most of the iodine activity, it was of considerable interest to determine if iodine activity would be present in the furnace off gases and whether this would give rise to an off-gas handling problem. Considerable iodine activity (about one-quarter of the total) was found condensed on the upper walls of the furnace chamber, but little iodine activity (about 0.1 percent of the total) was found in the furnace off gases (i.e., removed by a charcoal filter unit). No serious off-gas handling problem resulting from iodine is evident. Iodine disappeared from solution not only by volatilization but also by another mechanism, probably a drossing reaction.

Of the other fission products, ruthenium, as expected, largely accompanied uranium through the process, whereas the rare earths, yttrium, and barium and strontium appeared predominantly in the plutonium product solution. The bulk of the zirconium and tellurium activities were lost; only small percentages were found with either the uranium or plutonium product. It is believed that these activities were removed by sorption on solid surfaces.

Equipment has been erected for demonstration of the plutonium concentration step (effected by boiling off magnesium and zinc). It is expected that large-scale demonstrations of the blanket process (up to the point of solution boildown) will be carried out in the pilot plant (the "large-scale integrated equipment") for the skull reclamation process.

3. Other Liquid Metal Processes

Liquid metal processes for the purification of other fuels are also under development, with emphasis on fast breeder reactor cores. These fuels may be either alloys or refractory compounds of uranium and plutonium. Previously developed pyrometallurgical processes are generally incapable of effecting the required separation of plutonium from rare earth fission products in a fuel of this type.

Two potential methods for separating rare earth fission products from uranium and plutonium are being investigated. One involves differences in the distribution behavior of the elements of interest between liquid magnesium-zinc solution and molten fluxes which contain magnesium chloride. A separation of rare earths from uranium and plutonium appears possible, with the rare earths transferring selectively to the flux phase while the uranium and plutonium remain in the metal phase. The other method is based on the low solubility of uranium-plutonium mixtures and the relatively high solubility of rare earths in liquid calcium-zinc alloys.

a. Metal-Flux Distribution Studies

Further information has been obtained on the distribution behavior of pertinent elements between liquid magnesium-zinc alloy and molten magnesium chloride at 800 C. The distribution data are found to agree well with theoretical behavior that can be predicted from thermodynamic data recently obtained from liquid metal systems, and published free energies of formation, assuming the equilibrium reaction

Figure I-8
DISTRIBUTION OF SELECTED
ELEMENTS BETWEEN ZINC-
MAGNESIUM ALLOY AND
MAGNESIUM CHLORIDE

Temperature: 800 C
Mixing Rate: 300 rpm
Crucible: tantalum
Atmosphere: argon

Distribution coefficients, $K_d = (\text{w/o in flux})/(\text{w/o in metal})$, for a variety of individual elements of process importance are shown as a function of magnesium concentration in the metal phase in Figure I-8. In general, the rare earths, barium, and americium tend to favor the flux phase, while the other actinide metals and the noble metals appear in the metal phase. Since barium and samarium appeared only in the flux phase, distribution coefficients for these elements were not calculated. For most elements, the distribution coefficient decreases sharply, reaching a minimum at about 10 weight percent magnesium, then increases more slowly on further magnesium additions. The shape of the curves results mainly from the changing activity coefficients of the species in the metal phases which enter into Equation 1.

In a series of codistribution studies involving uranium, plutonium, and praseodymium, the distribution coefficients of these elements were in agreement with those obtained in experiments with the individual elements. Brief studies of the effects of several other variables were made. When the uranium concentration was increased from one weight percent to two weight percent, with 10 weight percent magnesium in the zinc, the

distribution coefficient for uranium increased approximately twofold. Between two and ten weight percent, the distribution coefficient increased only slightly. In the case of plutonium, the distribution coefficient increased only slightly as the plutonium concentration was raised from 0.5 to 4.8 weight percent.

Since the plutonium-praseodymium separation in this system is typical of the separation of greatest process interest and because these two elements are easily determined in the presence of each other, the effects of several variables were determined using these elements. For an equimolar lithium chloride-magnesium chloride flux and 50 weight percent magnesium in the zinc, the logarithm of the plutonium-praseodymium separation factor (ratio of distribution coefficients) decreased linearly as a function of the reciprocal absolute temperature. At 850 C the separation factor was 25 and at 620 C it was 47. When a magnesium chloride flux was diluted with lithium chloride at 800 C and with 50 weight percent magnesium in the metal phase, the distribution coefficients for plutonium and praseodymium both decreased gradually at first, then decreased rapidly at magnesium chloride concentrations below about 30 percent. At magnesium chloride concentrations above 25 mole percent, the separation factor remained constant at 33. At lower magnesium chloride concentrations, it decreased. A similar effect was observed when the magnesium chloride was diluted with cesium chloride or barium chloride. The separation factor was little affected on the addition of 10 mole percent magnesium fluoride to the magnesium chloride flux. Substitution of magnesium bromide for magnesium chloride in the flux increased the plutonium distribution coefficient by a factor of about 20, but had a negligible effect on the distribution coefficient for praseodymium. Thus the separation factor value decreased twentyfold. Substitution of cadmium for zinc in the metal phase at 650 C had little effect on the separation factors of plutonium and praseodymium.

Table I-7 lists separation factors for several pairs of elements for which separation procedures are of practical interest. The data in this table are for a temperature of 800 C and 50 weight percent magnesium in the magnesium-zinc phase. It can be seen from the data that substantial separation factors are available for the removal of rare earth fission products from uranium and plutonium, as well as thorium. Stage calculations have shown that in order to remove 90 percent of the praseodymium and recover 99 percent of the uranium and plutonium from an irradiated fuel, two extraction and two scrub stages would be adequate. Since the plutonium-praseodymium separation factor is lower than those for plutonium and most of the other rare earths, somewhat higher removals would be obtained for the rare earth fission products as a group. It is of interest to note that americium is the only actinide metal which favors the flux phase in these systems, thus making possible a separation of americium from the other actinide metals.

Table I-7

SELECTED SEPARATION FACTORS OF
PROCESS IMPORTANCE

Temperature: 800 C
Metal Phase: 50 w/o Mg-50 w/o Zn
Flux Phase: MgCl_2

Element Pair	Separation Factor ^a
Yttrium-Plutonium	74
Cerium-Plutonium	44
Praseodymium-Plutonium	35
Americium-Plutonium	29
Yttrium-Uranium	204
Cerium-Uranium	128
Praseodymium-Uranium	95
Plutonium-Uranium	2.7
Americium-Curium	34
Plutonium-Curium	1.2
Yttrium-Thorium	837
Praseodymium-Thorium	392
Plutonium-Thorium	12
Uranium-Thorium	4.2

^aThe separation factor is the ratio of the distribution coefficients for the two elements under these conditions.

b. Separation of Zirconium from Uranium and Plutonium

Current processing schemes provide for the separation of plutonium-uranium from the noble metal fission products (niobium through ruthenium, but not zirconium) by reaction with a molten mixture of zinc and a chloride flux containing an oxidant such as zinc chloride. Plutonium, uranium, zirconium, and Group IA, IIA, and IIIA fission products are oxidized into the salt phase, whereas noble metals either dissolve or are precipitated in the zinc phase. In principle, zirconium can be quantitatively transferred to the metal phase with little loss of uranium and plutonium (less than one percent each) by careful titration of zinc and zirconium chlorides with a reductant. The reduction may be chemical (e.g., with magnesium metal) or electrical.

The feasibility of the chemical concept was tested, employing a plutonium/uranium ratio of approximately 1:100. (A typical power breeder reactor fuel would probably contain 10 to 20 weight percent plutonium.) A lithium chloride-potassium chloride eutectic mixture containing one weight percent lithium fluoride as well as plutonium,

uranium, zirconium, and zinc chlorides was titrated at 550 C with cadmium-5 weight percent magnesium in the presence of excess cadmium-

Figure I-9

TITRATION OF THE CHLORIDES OF PLUTONIUM, URANIUM, ZIRCONIUM, AND ZINC WITH MAGNESIUM METAL

Crucible: Alumina
Stirrer: Tantalum
Temperature: 550 C
Metal Phase: ~700 g Cd-6 w/o Zn
Salt Phase: ~475 g LiCl-KCl-LiF
Metal (millimoles): Pu - 4.2
U - 400
Zr - 14
Zn - 114

6 weight percent zinc. The experimental conditions and the course of the titration are shown in Figure I-9. The results indicate, for example, that 92 percent of the zirconium could be reduced into the metal phase accompanied by only 1 percent of the plutonium and 1.4 percent of the uranium. However, careful control is required to minimize plutonium and uranium losses. For plant-scale practice, potentiometric techniques employing indicator electrodes might provide close control of the reduction.

c. Calcium-Zinc Separations Process

The separation of rare earth fission products from uranium and plutonium in this scheme is accomplished by first oxidizing the fuel constituents into a molten halide flux, then reducing the uranium, plutonium, and rare earths by means of a molten calcium-zinc solution. Plutonium and uranium precipitate out of the solution, while the rare earth elements remain in the solution.

In a scouting experiment, uranium and plutonium chlorides dissolved in lithium chloride-potassium chloride eutectic containing one percent lithium fluoride were contacted with a zinc-66 weight percent calcium solution. The uranium and plutonium were both reduced completely from the molten salt phase, and 95 percent

of the plutonium and 99.9 percent of the uranium precipitated. Previous work had shown that cerium, used as a stand-in for all the rare earth fission products, remains in the liquid metal solution under these conditions. Therefore, a separation of the rare earths from uranium and 95 percent of the plutonium can be effected by removing the supernatant liquid metal from the precipitated metals. However, five percent plutonium loss to the

supernatant liquid metal phase is unacceptably large for process purposes. Further studies are being conducted on this system in an effort to find conditions under which this loss can be reduced to an acceptable level of one percent or less.

As a part of this study, the individual solubilities and co-precipitation behavior of uranium and plutonium in calcium-zinc solutions are being investigated. Solubility data determined thus far for uranium are presented in Figure I-10. These solubility curves resemble those for uranium in magnesium-zinc solutions with respect to their general shape, but the absolute solubility values are considerably lower in the calcium-zinc system.

Figure I-10
SOLUBILITY OF URANIUM IN ZINC-CALCIUM SOLUTIONS

During the course of these studies, it became apparent that current literature information on the calcium-zinc phase diagram was inaccurate. Figure I-11 is the result of a redetermination of this diagram by thermal analysis techniques supplemented by X-ray diffraction and effusion balance data.

Figure I-11
CALCIUM-ZINC PHASE DIAGRAM

4. Supporting Engineering Studies

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

a. Studies of Mass Transfer in Liquid Metal Systems

Fundamental investigations of mass transfer are underway in two areas: (1) study of mass transfer in agitated liquid metal systems, and (2) study of mass transfer in a flowing metal system at Reynolds numbers approaching 200,000. In the latter study, which is the subject of a PhD thesis by a research associate from Ohio State University, $\frac{1}{2}$ -in. diameter

uranium spheres are dissolved at 500 C in flowing cadmium in a loop system fabricated of $1\frac{1}{2}$ -in. stainless steel (Type 304) pipe. The data have been accumulated and are now being analyzed.

In the mass transfer experiments in an agitated metal system, small uranium cylinders are being dissolved at 500 C in cadmium in a baffled 5-in. ID steel tank. The uranium right cylinders (two sizes, 7-mm diameter, 7-mm long and 4-mm diameter, 4-mm long, each size being used in separate experiments) were cut from cast uranium rods so that crystal orientation would be random. They were wetted with zinc prior to use to insure an oxide-free surface for dissolution.

Solution rate coefficients obtained to date are presented in Figure I-12. The integrated mean solution rate coefficient, k_m , expressed as gram-atoms solute/(min)(sq cm of interfacial area)(g solute/g solvent), is plotted against the agitator speed. Ultimately, it is hoped that the data can be correlated by dimensionless groups to provide greater utility for scale-up or for application to other systems.

Figure I-12

SOLUTION-RATE COEFFICIENTS FOR PARTICULATE URANIUM SUSPENDED IN AGITATED CADMIUM

5-in. x 5-in. cylindrical baffled tank
2.5-in. 45° pitched paddle, 0.6-in. face,
deflecting downward

The data in Figure I-12 show two regimes of solution speeds for the 7-mm cylinders. In one regime of slow solution rates at stirring rates of 400 rpm and below, the cylinders are not suspended but may be in motion on the bottom of the tank. In the other regime of appreciably faster solution rates at stirring speeds above about 500 rpm, suspension of cylinders begins, with the degree of suspension increasing with stirring speed. Presumably, there is a transition region between these regimes. In both regimes, the rate of solution increases with increasing stirrer speed.

b. Diffusivity of Uranium in Liquid Metal Solvents

The diffusivity of uranium has been determined as a function of temperature in cadmium, zinc, bismuth, and aluminum. These liquid metals are frequently used as solvents for uranium. A diffusivity measurement in cadmium was made to permit correlation of mass transfer data now being obtained for the dissolution of uranium in cadmium. The measurements were extended to the other liquid metal systems because of the virtual absence of uranium diffusivity data in these systems

and also to expose possible trends or correlations of uranium diffusivities with solvent metal properties.

Figure I-13

DIFFUSIVITIES OF URANIUM IN VARIOUS SOLVENT METALS

A capillary bath technique was employed for determining uranium diffusivities. A capillary tube (about $\frac{3}{16}$ -in. inside diameter and 1-in. long) closed at the lower end and containing a known high concentration of uranium in the liquid metal solvent of interest was immersed in a solvent metal bath containing a very low concentration of uranium. The uranium was allowed to diffuse from the upper open end of the capillary tube into the bath for a predetermined time. The diffusivity value was then calculated from the initial and final concentrations of uranium in the tube and the temperature and duration of the diffusion.

The diffusivity data that were obtained are shown in Figure I-13. All diffusivity values are lower than would be calculated by the Einstein-Stokes equation using a value of $1.421 \text{ \AA}$ for the radius of the uranium atom. This suggests that the diffusing

species in each case is a coordinated complex of uranium and solvent atoms. The data at 500 C in bismuth are in good agreement with a value reported by Bonilla¹ of 2.24 sq cm/day (2.59×10^{-5} sq cm/sec). This is the only value for these systems found in the literature.

c. Natural Convection Heat Transfer in Liquid Metals

Work has been started to obtain experimental measurements of natural convection heat transfer rates in liquid metals. The data obtained will be compared with values calculated by the use of available theories. Theoretical calculations seem to be on very firm ground in the area of laminar flow natural convection for fluids whose Prandtl numbers* are of the order of one. However, outside of this area (for example, for fluids such as liquid metals whose Prandtl numbers are much different from one), there are practically no analytical results or experimental data. The experimental equipment for this study has been built, and experimental work using mercury as a representative liquid metal is now getting underway.

d. Mixing of Liquid Metals

During the past year, a dynamometer was constructed to measure mixing power inputs to liquid metal and other process systems of interest. Power inputs were determined by measuring the reaction torque on the agitator motor, which was suspended by a torsion wire. The mixing power correlations reported in the literature for aqueous and organic systems were found to be applicable to liquid metals. The dynamometer is now being employed to determine the degree of agitation required in various process operations, e.g., reduction of uranium or thorium oxides in molten salt-metal systems.

e. Liquid Metal Boiling Studies

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

Vaporization from the liquid-vapor surface of a liquid pool without the formation of vapor bubbles (here called nonturbulent vaporization) is essentially an entrainment-free method of vaporization. In contrast, the vapor bubbles which break through the surface in normal nucleate, transition and film boiling generally create droplets of liquid

¹C. F. Bonilla, Mass Transfer in Molten Salt and Metal Systems, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. IX, P/122, p. 338, United Nations, New York (1956).

*Prandtl number is $C_p \mu / k$ where C_p is heat capacity at constant pressure, μ is viscosity, and k is thermal conductivity, all in consistent units.

which can be entrained by the vapor stream. If high enough vaporization rates of liquid metals could be achieved by nonturbulent vaporization, this technique would be useful (for example, in boiling down the plutonium-magnesium-zinc product solution of the blanket process).

The factors affecting the nonturbulent vaporization of mercury are being studied in glass apparatus. Vaporization rates up to 115,000 Btu/(hr)(sq ft) have been achieved at pressures of 1 to 10 mm of mercury by using conditions which promote the transport of heat to the surface (e.g., stirring, or the use of geometries conducive to natural convection).

(2) Performance of Large-Scale Cadmium-Distillation Unit

The large-scale cadmium distillation unit was operated intermittently during the past year. This unit, which is capable of distilling cadmium at rates of up to 100 kg/hour, has provided valuable experience in the large-scale handling of reactive liquid metals.

At one time in the past year, it was found that distillation rates were being limited by overheating of the radiation-cooled copper induction coil. This difficulty was traced to reduced emissivity of the copper coil, resulting from decomposition of a copper oxide coating and the formation of a shiny, low-emissivity metal surface. An appreciable reduction in coil-operating temperature and restoration of the ability to achieve high distillation rates were effected by coating the coil with aluminum oxide to increase its emissivity.

By the addition of tin, a nonvolatile solute, to cadmium charges, it has been found that several percent of the liquid cadmium is being entrained in the cadmium vapor. It is planned to install a standard de-entrainment unit in the vapor space above the boiling cadmium and evaluate its performance. Also, an inductance level gauge will be installed for measurement of the liquid level in the boiler. Successful operation of these devices will remove the last remaining problems encountered in the operation of this unit.

5. Preparation of Compounds in Liquid Metal Media

Pyrometallurgical procedures offer considerable promise as simple, economical methods for producing nuclear fuel materials. For example, metallic materials can be prepared by the direct reduction of actinide oxides, chlorides, or fluorides from a molten halide flux by liquid metal solutions containing magnesium. Pyrometallurgical procedures are also being considered for the preparation of refractory compounds,

such as carbides and sulfides of the actinide elements, which are attracting considerable interest as high-performance reactor fuels because of their resistance to damage by high temperatures and extensive irradiation. One method of preparing fuels of this type consists of adding carbon, silicon, or other elements to liquid metal solutions of the actinide metals. The product precipitates from solution and is recovered by suitable phase separation and retorting techniques.

a. Preparation of Uranium and Plutonium Carbides

In previous work it was found that uranium monocarbide, a promising fuel material, can be prepared by the addition of carbon to a zinc-magnesium solution of uranium at 750 to 800 C. The resulting product, which precipitates from the solution, has proved to have excellent pressing and sintering properties. In additional work, the technique has been refined, and uranium carbide has been prepared consistently that has carbon to uranium ratios within 5 percent of those in the charge material. Cold pressing and sintering of the powdered product has given pellets with densities as great as 90 percent of theoretical. Powders prepared by different methods from other sources gave similar densities when compacted by the same method. Control of stoichiometry and elimination of oxygen contamination are the most important problems.

Equipment has been constructed in which uranium monocarbide can be prepared in 0.5-kilogram batches by this method, with all operations taking place under vacuum or high-purity inert atmospheres. This facility (Figure I-14) is being used to produce well-characterized material for fabricability and irradiation studies by the Metallurgy and Reactor Engineering Divisions.

Facilities (Figure I-15) have also been installed for investigations of various methods for preparing plutonium carbides. These facilities are required to handle highly alpha-active materials and maintain high-purity inert atmospheres. Equipment installed includes a large nitrogen-filled glovebox which is used to investigate reactions for the preparation of plutonium carbide. Reactions will be made to occur inside sealed vessels. Connected to the large box by a vacuum interlock is a smaller glovebox where reaction vessels are loaded and unloaded and the products will be handled. This smaller box has an atmosphere of purified helium which is purified by being passed through a molecular sieve drier and an activated charcoal bed cooled with liquid nitrogen. The equipment has been tested, and the investigation of various methods for the preparation of plutonium carbides in quantities up to about 50 grams is expected to be underway shortly.

Figure I-14

VACUUM-INERT GAS GLOVEBOX FOR URANIUM
MONOCARBIDE PREPARATION

End view, showing control panel.

Side view, showing viewing windows, covered glove ports, and one of three furnaces (on cart) which may be raised and bolted to the bottom port of the glovebox.

Several new techniques which may prove useful for the preparation of carbides are being examined. For instance, preliminary studies indicate that uranium monocarbide is formed by the reaction of methane with uranium-zinc intermetallic compounds at temperatures of 600 to 800 C.

b. Preparation of Uranium and Plutonium Sulfides

Uranium monosulfide has been prepared on a 20-gram scale by the reaction of hydrogen sulfide with powdered uranium formed by a hydriding-dehydriding procedure. In recent preparations, the impurity content of the product (mainly oxides and oxysulfides) has been reduced to less than 0.1 percent.

Figure I-15

PLUTONIUM CARBIDE FACILITY

A large nitrogen-filled glovebox at the left is connected by the interlock at the extreme left to another glovebox (not shown) and by a cylindrical vacuum interlock to the helium-filled glovebox at the center. The helium-purification equipment is at the right.

The laboratory-scale equipment used in preparing uranium monosulfide is designed so that it can be readily converted to studies of plutonium sulfides. Other facilities capable of producing 0.5-kilogram batches of uranium monosulfide for fabricability and irradiation studies have recently been placed in operation.

c. Direct Preparation of Uranium Metal from Ore Concentrates

A new process for preparing uranium metal directly from ore concentrates by zinc-magnesium reduction is being investigated. First, the noble metal impurities in the ore concentrate are converted to chlorides and volatilized from the flux-ore concentrate mixture. The chlorination is brought about by air oxidation of magnesium chloride in the flux. The composition of the flux has proved to be of great importance in achieving rapid and complete reduction. Effective flux compositions have been found within the ternary system, calcium chloride-magnesium chloride-magnesium fluoride. In the next step the uranium is reduced to the metal by magnesium in

zinc. During this step, electropositive impurity elements such as sodium and calcium remain in the flux while reduced uranium metal appears in solution in the metal phase. The flux phase is then removed, after which the zinc and magnesium are separated from the uranium product by vacuum distillation.

In preliminary studies using the procedure described above, it was found that all the significant impurities in the ore concentrate except silicon were separated from the uranium product. Later work showed that silicon can be removed from the ore concentrate by a simple pretreatment with ammonium bifluoride, which converts silica to the volatile tetrafluoride. A scheme for the preparation of uranium metal which incorporates the preceding steps is shown in Figure I-16. When a typical ore concentrate (Anaconda resin-in-pulp ion-exchange type) was carried through these steps in a laboratory demonstration experiment, the purity of the final arc-melted uranium product was over 99.9 percent, and the silicon content was 170 ppm. This product was close to reactor-grade specifications. Successful development of a process of this type would eliminate several purification and chemical conversion steps and may well be simpler with fewer recycle problems than the present method for producing natural uranium metal from uranium ore concentrate.

Figure I-16

PROPOSED SCHEME FOR THE PRODUCTION OF URANIUM METAL

d. Direct Reduction of Thorium Dioxide

The reduction of thorium dioxide to the metal by means of the liquid metal-flux technique was also studied. The work was aimed mainly at the selection of flux systems that result in complete reduction of thorium dioxide, with consideration given to reagent costs. The investigations revealed that satisfactory reductions of thorium dioxide by zinc-5 weight percent magnesium could be obtained at 750 C in the calcium chloride-magnesium chloride-calcium fluoride system over a considerable range of flux compositions. The amount of thorium dioxide used in the runs was such that the

thorium concentration in the alloy would be one percent upon complete reduction. This value is below the saturation solubility of thorium in zinc (approximately 1.23 weight percent at 750 C), thus preventing segregation of thorium-zinc intermetallic. The solubility of thorium in magnesium-zinc solutions is shown in Figure I-17.

The data (see Figure I-18) showed a systematic relationship between the constituents and composition of the flux systems and their

Figure I-17

SOLUBILITY OF THORIUM IN MAGNESIUM-ZINC SOLUTIONS

Flux: $\text{CaCl}_2\text{-MgCl}_2\text{-CaF}_2$
 Time: 4 hr or less
 Temperature: 750 C
 Mixing Rate: 800 rpm
 Metal Phase: 600 g Zn-5 w/o Mg
 Thorium Conc. in Metal Phase at
 Complete Reduction: 1 w/o
 (All points shown indicate >99 percent reduction.)

Figure I-18

EFFECT OF FLUX COMPOSITION ON THE REDUCTION OF THORIUM DIOXIDE

(For Conditions, see lower left of page)

effectiveness in the reduction of thorium dioxide. A minimum magnesium concentration of 11 atom percent of the cations at a fluoride ion concentration of 10 atom percent of the anions seems essential for quantitative reduction of thorium dioxide to the metal.

A tentative scheme for the production of thorium metal by this procedure is shown in Figure I-19.

Figure I-19

PROPOSED SCHEME FOR THE
PRODUCTION OF THORIUM METAL.

e. Reduction of Plutonium Dioxide

Recent laboratory studies have shown that plutonium dioxide may be reduced to the metal by the same techniques used for uranium and thorium. For plutonium, the composition of the flux is much less important in obtaining satisfactory reduction. The principal advantages of a process of this type for the preparation of plutonium metal are: (1) nearly complete elimination of plutonium losses and (2) a substantial reduction in the neutron hazard, since the (α, n) reaction is much less efficient in plutonium oxides than in the fluorides.

6. Chemistry of Molten Salts

Since molten salts, as well as liquid metals, are being used as media for pyrometallurgical process steps, the chemistry of molten salt systems is being studied to supply supporting information for process use and to contribute to an understanding of the principles involved. Magnesium chloride is a key constituent in nearly all of the molten salt systems being considered for process use. Physical and chemical investigations of molten salts have therefore centered mainly around various systems which contain magnesium chloride.

a. Phase Diagram of the System, Lithium Chloride-Magnesium Chloride

Differential thermal analysis, supplemented by results of optical microscopy and by X-ray diffraction data, has been used to establish the phase diagram for the lithium chloride-magnesium chloride system. The final version of the phase diagram is shown in Figure I-20.

Figure I-20

LiCl-MgCl₂ PHASE DIAGRAM

The results indicate the existence of a continuous series of solid solutions across the entire composition range. The major differences between this diagram and that reported in the early literature are that this work shows higher liquidus and solidus curves and a relocation of the minimum from 40 to 33 mole percent magnesium chloride. The lower temperatures reported in the literature are attributed to impure materials.

b. Spectrophotometric Studies of Uranium Compounds in Molten Chloride Solutions

High-temperature spectrophotometric techniques are being utilized to investigate the reactions of uranium oxides in molten chloride solvents. When uranium oxides are added to molten chloride solutions, measurements in the visible and near-infrared regions show a

unique spectrum which is attributed to a uranium (V) species, UO_2^+ . This species is of particular interest, since it is not ordinarily possible to obtain stable pentavalent uranium species in solution. This same spectrum has been produced through additions of uranium trioxide, uranous oxide, magnesium uranate, or uranyl chloride to molten chloride solvents at temperatures above 600 C.

The addition of higher uranium oxides to salts containing magnesium chloride results in the formation of magnesium uranate and uranyl chloride

The magnesium uranate, in turn, reacts further to produce more uranyl chloride

At temperatures above about 600 C, uranyl chloride undergoes thermal decomposition, forming the uranium (V) species mentioned previously

Formation of the uranium (V) species is favored by raising the temperature above 600 C and by removing chlorine from the system. Addition of chlorine has been shown to cause reaction 3 to reverse.

Representative examples of the UO_2^+ spectrum in two different molten chloride solvents are shown in Figure I-21. In order to

Figure I-21

SPECTRA OF UO_2^+ IN TWO MOLTEN CHLORIDE SOLVENTS

determine the molar absorptivities, a known amount of uranyl chloride was added to the molten chloride solvent; then the quantity of chlorine evolved by reaction 3 and the change in optical absorbance were measured simultaneously as chlorine was removed from the spectrophotometer cell.

Confirmation of the chemical evidence that the spectrum results from the UO_2^+ ion has been obtained by comparing the spectrum with the published spectrum of neptunium (VI) NpO_2^{++} in deuterium perchlorate. The optical absorption of both species results from a single 5f electron. The two spectra show a marked resemblance. Each peak in the neptunyl spectrum is at a higher energy than the corresponding uranium (V) peak by a nearly constant factor.

C. Chemistry of Liquid Metals

The chemistry of liquid metal solutions is being studied to provide basic concepts and data for the design of pyrometallurgical separations processes. In addition, these studies are contributing to our understanding of liquid metal solutions.

1. Phase Studies

All of the pyrometallurgical processes being developed involve the use of metallic solutions. Consequently, it is necessary to know the solid-liquid phase relations of a large number of different binary and ternary metallic systems. The liquidus has been exactly determined by solubility measurements for the majority of systems of importance in the process development work. The solid phases in equilibrium with the saturated solutions have been determined by isolation of the phases from solubility ingots, followed by X-ray identification; by direct synthesis of the solid phases from the component metals, followed by X-ray characterization; and by the use of the continuous recording effusion balance, supplemented by X-ray identification. In a few instances thermal analysis methods have been used to supplement the solubility studies.

The continuous recording effusion balance, when supplemented by X-ray diffraction identification, has proven to be a very powerful technique for the elucidation of complex phase diagrams. This method is applicable to binary systems where one of the components is much more volatile than the other. This method has been used to clarify the phase relations in the binary systems of zinc with the rare earth metals lanthanum, cerium, praseodymium, and neodymium. Alloys of the rare earth metals and zinc, which contained zinc in excess of the amount necessary for the formation of the most zinc-rich phase, were prepared by reacting the components at 900 C, annealing at 500 C, and quenching to room temperature. The partial pressure of zinc in powdered samples of these alloys was determined by measuring the rate of effusion as a function of composition. A representative isotherm for the praseodymium-zinc system is shown in Figure I-22. The horizontal portions of the curve represent two-phase regions, the sharp vertical portions represent changes from one two-phase region to another two-phase region, the rounding of the curve between horizontal and vertical portions represents a nonequilibrium condition, where the rate of diffusion within the solid is unable to maintain the equilibrium vapor pressure. The abscissa of the vertical portion of the curve represents the composition of the phase which is decomposing to form a new phase during the next horizontal portion of the curve. The small dips are attributed to the delayed nucleation of the new phase.

Figure I-22

PRASEODYMIUM-ZINC SYSTEM.
EFFUSION ISOTHERM AT 531 C

In separate experiments, the effusion was stopped at several places along each horizontal curve and the residual alloy examined by X-ray diffraction. By this means the phases present in each two-phase region were identified or characterized depending on whether or not the X-ray diffraction patterns had been previously reported.

The phases observed for the four light rare earth metal-zinc systems are given in Table I-9. Common to all four systems are the intermetallic compounds having the compositions $MZn(CsCl, B-2 \text{ type})$, MZn_2 (unknown structure), $MZn_{\sim 7}$ (unknown structure), M_2Zn_{17} (hexagonal structure similar to ϵ - U_2Zn_{17}) and MZn_{11} (body-centered tetragonal, $BaCd_{11}$ type). Only lanthanum forms the phases $LaZn_4$ (unknown structure) and $LaZn_{13}$ (face-centered cubic $NaZn_{13}$ type). Only neodymium forms the phase $NdZn_{12-x}$ (structure similar to ϵ - UZn_{12-x}). This latter phase is found only in the neodymium-zinc system when alloy preparations are made at high temperatures.

Neodymium alloys prepared at about 500 C contained only the $NdZn_{11}$ phase. The phases MZn_3 , $MZn_{3.6}$ and $MZn_{4.3}$ are of unknown structure and are not observed in the lanthanum-zinc system. The stability of $MZn_{5.25}$ phase ($CaCu_5$ type) appears to decrease in relation to adjoining phases as one progresses from lanthanum to neodymium.

Table I-9

INTERMETALLIC PHASES FOUND IN
La-Zn, Ce-Zn, Pr-Zn AND Nd-Zn SYSTEMS

Lanthanum	Cerium	Praseodymium	Neodymium
$LaZn_{13}$	-	-	-
-	-	-	$NdZn_{12-x}$
$LaZn_{11}$	$CeZn_{11}$	$PrZn_{11}$	$NdZn_{11}$
$LaZn_{8.5}$	$CeZn_{8.5}$	$PrZn_{8.5}$	$NdZn_{8.5}$
$LaZn_{7.25}$	$CeZn_7$	$PrZn_7$	$NdZn_{6.5}$
$LaZn_{5.25}$	$CeZn_{5.25}$	$PrZn_{5.25}$	-
-	$CeZn_{4.4}$	$PrZn_{4.3}$	$NdZn_{4.3}$
$LaZn_4$	-	-	-
-	$CeZn_{3.6}$	$PrZn_{3.6}$	$NdZn_{3.5}$
-	$CeZn_3$	$PrZn_3$	$NdZn_3$
$LaZn_2$	$CeZn_2$	$PrZn_2$	$NdZn_2$
$LaZn$	$CeZn$	$PrZn$	$NdZn$

Figure I-23

SOLUBILITIES OF ELEMENTS WITH
ATOMIC NUMBERS 55 THROUGH
62 IN ZINC AND CADMIUM

The solubilities of the light rare earth metals in liquid zinc have been measured by chemical analysis of filtered samples of the equilibrium liquid phase. In Figure I-23 the solubilities of these elements in zinc at 550 C are shown as a function of atomic number. For comparison, the solubilities of the same elements in liquid cadmium (at 400 C) and of barium in liquid zinc are also shown. In the case of cadmium as the solvent, the equilibrium solid phase is the same cubic BaHg_{11} type for each of the rare earth metals shown. The solubility is seen to increase in a regular fashion with increasing atomic number. For these dilute solutions, the solubility is given by the equation

$$\log x = \frac{\Delta F_f^0}{2.3 RT} - \log \gamma_M$$

where x is the atom fraction of rare earth metal in the saturated liquid solution, ΔF_f^0 is the free energy of formation of the intermetallic compound in equilibrium with the solution, and γ_M is the activity coefficient of the rare earth metal in the liquid solution. The regular variation of $\log x$ with atomic number implies that both ΔF_f^0 and γ_M smoothly vary with increase

in atomic number. The similarity of the decomposition pressures of the MCd_{11} compounds (effusion studies not yet completed) suggests that the increase in the solubility with increasing atomic number is related mainly to the increase in the activity coefficients with increasing atomic number.

In the case of the solubilities of the light rare earth metals in zinc, no smooth and regular increase in solubility with increasing atomic number is observed. This no doubt is due to the fact that different types of intermetallic compounds are formed as equilibrium phases with zinc as the solvent. Examination of the solubility ingots showed that the phases in equilibrium with the solutions were BaZn_{13} and LaZn_{13} (cubic NaZn_{13} type), CeZn_{11} and PrZn_{11} (tetragonal BaCd_{11} type) and NdZn_{12-x} (epsilon UZn_{12-x} type). Since these phases differ in structure and stoichiometry, it would not be expected that their free energies of formation would be a simply related function of atomic number alone. It is of interest that the phase separating from solution in the case of neodymium is the high temperature phase NdZn_{12-x} rather than the low temperature NdZn_{11} phase. In view of the fact that the solubility of NdZn_{12-x} is somewhat greater than that which would be estimated from a linear extrapolation of the data for CeZn_{11}

and PrZn_{11} , it is possible that the stable phase is NdZn_{11} at 550 C. It is interesting to note that the difference in free energy of formation between NdZn_{12-x} and NdZn_{11} as estimated from the solubilities would be only 200 calories. Thus, only a very small difference in free energy is needed to stabilize one phase over another.

The technetium-zinc system is being studied by a combination of solubility measurements, thermal analysis and effusion. The solubility was found to vary from 0.002 weight percent at 470 C to 0.12 weight percent at 758 C. The solubility curve showed a break at 544 C, thereby suggesting a peritectic reaction at this temperature. Two different intermetallic phases have been found. Their structures have not yet been established but their compositions are about TcZn_5 and TcZn_{15} .

As an aid in the interpretation of data for the distribution of metals between the partially immiscible pair lead and zinc, the mutual solubilities were measured over the range 648 to 795 C. This range had not been well defined by direct measurement. By direct measurement of the compositions of phases in equilibrium it has been established that the consolute temperature lay between 784 ± 20 and 789 ± 2 C. This is in good agreement with previous investigators who found 770 to 800 C by an X-ray absorption method and 798 C by an extrapolation of cooling curve data. The liquid composition at the consolute point is about 61 weight percent lead and 39 weight percent zinc.

2. Thermodynamic Studies

The thermodynamic properties of key elements in liquid metal solutions are being determined by the use of high-temperature galvanic cells. The plutonium-zinc system has been studied using a cell of the form

The cell reaction for the temperature range studied (421 to 640 C) is

The emf as a function of temperature for two different cells is shown in Figure I-24. The following quadratic equation was found to fit the data best:

$$E(\text{volts}) = 0.9591 - 0.3664 \times 10^{-3} T - 0.1685 \times 10^{-6} T^2 \quad .$$

From this equation and the solubility of plutonium in the saturated solutions, the thermodynamic quantities for the plutonium-zinc system summarized in Table I-10 were computed.

Figure I-24

EMF VS TEMPERATURE
 CELL: Pu/PuCl₃, KCl-LiCl (EUTECTIC)/
 Pu-Zn (TWO PHASE ALLOY)

Table I-10

THERMODYNAMIC FUNCTIONS - PLUTONIUM-ZINC SYSTEM 450 C

$$\Delta G_f^0 = -42.0 \text{ kcal/mole}$$

$$\Delta H_f^0 = -72.5 \text{ kcal/mole}$$

$$\Delta S_f^0 = -42.2 \text{ cal/deg mole}$$

$$\bar{L}_{\text{Pu}} = -46 \text{ kcal/mole}$$

$$\bar{S}_{\text{Pu}}^{\text{xs}} = -25 \text{ cal/mole}$$

great utility for the testing of theories of metallic solutions. A study of the chemistry of liquid alkali metals has been started to furnish basic data and concepts to aid in the solution of practical problems which arise in the use of liquid alkali metals.

3. Chemistry of Alkali Metals

The alkali metals are finding increased use as heat transfer media and working fluids for power reactors and power sources for space use. This is particularly true for fast power reactors for which liquid alkali metals are the only practical choice for the primary coolant. In addition, the alkali metals are among the simplest and most metallic of the elements; thus, their properties offer

A practical problem in the use of liquid sodium is caused by the tendency of ferrous alloys to carburize or decarburize when exposed to liquid sodium. Liquid sodium is able to act as a medium for the transfer of carbon from regions of high thermodynamic activity to regions of lower activity. The unraveling of the mechanism for the transfer of carbon via liquid sodium is the first problem which is being attacked.

To do significant chemical work using liquid alkali metals requires metals of known purity. This involves both purification and analysis. In the particular studies being undertaken the carbon and oxygen content of the sodium is of particular importance. Accurate analytical methods for these impurities in concentrations below 100 ppm do not presently exist. It is believed that the accuracy of present methods for carbon can be improved at low levels by the use of carbon-14 labeled carbon in the experimental work. Two radiochemical methods are being explored for the analysis of oxygen in sodium. The first method involves fast neutron irradiation of the sample to produce nitrogen-16 which is counted. The second method involves the production of fluorine-18 from the contained oxygen using tritons. The tritons are produced in situ by the reaction of thermal neutrons on a small amount of lithium added to the sodium, i.e., by the $\text{Li}^6(n,T)\text{He}^4$ reaction. Preliminary experiments indicate that the first method is usable down to the 10 ppm range and may go to 1 ppm. Theoretical computations indicate that the second method will be usable down to 1 ppm.

In addition to these practically oriented studies, two studies of somewhat more theoretical nature are underway. Surprisingly little direct experimental data exist on the thermodynamics of binary solutions of alkali metals. The fact that the elements in several of the pairs (viz., Li-Na, Li-Cs) are immiscible suggests that the deviations from ideal behavior may be large. However, many of the pairs of heavier elements form completely miscible liquids which would suggest smaller deviations from ideal behavior. A study of the thermodynamics of the sodium-potassium system by the use of a vapor pressure method has been started. In this method the absorption of light at the atomic resonance wavelengths will be measured for each of the elements in the equilibrium vapor phase over the liquid.

The interaction of nonmetallic atoms with metals offers an opportunity to study the electronic configuration of metals when perturbed. A study has been begun on the solubilities of the rare gases in liquid alkali metals. In this study the solubilities and their temperature coefficients will be measured. This will permit the computation of the partial molal quantities of rare gas atoms in liquid alkali metal solutions.

4. Magnetic Susceptibility Studies

The bulk magnetic susceptibilities of the intermetallic compounds CeCd_{11} , NdCd_{11} , ThCd_{11} and UCd_{11} were measured by the Faraday Method from approximately 2 K to 300 K. These compounds are isomorphous and have a known crystal structure (BaHg₁₁ type CeCd_{11} $a_0 = 9.319 \text{ \AA}$; NdCd_{11} $a_0 = 9.294 \text{ \AA}$; ThCd_{11} $a_0 = 9.274 \text{ \AA}$; UCd_{11} $a_0 = 9.289 \text{ \AA}$). The magnetic properties of 4f and 5f atoms in intermetallic compounds with chemical environments that are almost identical can be studied by means of this series.

The susceptibility of the three compounds CeCd_{11} , NdCd_{11} and UCd_{11} were found to obey a Curie-Weiss law ($\chi = \frac{C}{T + \Delta}$) from about 4.2 K to room temperature. Values of the Curie constant C , the Weiss Δ , and the effective Bohr magneton number for each system are given in the table below. The susceptibility of ThCd_{11} was found to be temperature independent.

Compound	Curie Constant, C (emu-deg/mole)	Weiss Δ (K)	Effective Bohr Magneton Number
CeCd_{11}	0.811	2	2.55
NdCd_{11}	1.668	8	3.64
UCd_{11}	1.798	41.5	3.81

The electronic configuration of both cerium and neodymium in their alloys was determined unambiguously from the experimental moments. The experimental magnetic moments of $2.55 \mu_B$ (Bohr magnetons) for cerium is in good agreement with the theoretical value of $2.56 \mu_B$ for a system with one unpaired spin ($4f^1$ configuration, $^2F_{5/2}$ ground state). Similar agreement exists between the experimental moment of $3.64 \mu_B$ for Nd in its alloy and the theoretical moment of $3.62 \mu_B$ for a system with three unpaired spins ($4f^3$ configuration $^4I_{9/2}$). The electronic configuration for uranium in UCd_{11} , however, could not be determined purely from the measured moments. The closeness of the theoretical moments for $5f^2$ and $5f^3$ configurations which are $3.58 \mu_B$ and $3.62 \mu_B$, respectively, makes a clear-cut choice between these two configurations difficult. A decision in favor of a $5f^2$ configuration for uranium was based on the observation that below 4.2 K, the susceptibility became temperature independent. On the assumption that this low temperature magnetic behavior arises from crystal field interactions rather than exchange interactions, the temperature independent susceptibility must arise from a non-degenerate ground state; this situation is possible only for an even number of unpaired electrons (Kramer's rule).¹ Calculations have shown that a reasonable single parameter fit to the experimental curve for uranium is obtained by an overall crystalline field splitting of the 3H_4 multiplet of 220 cm^{-1} .

The absence of a temperature dependent paramagnetism in the ThCd_{11} system indicated that there are no localized unpaired electrons in this alloy. The electronic configuration for thorium therefore is probably $5f^0$.

It is concluded that the valencies of cerium and neodymium are three in CeCd_{11} and NdCd_{11} , respectively, and that the valencies of thorium and uranium in their alloys ThCd_{11} and UCd_{11} , respectively, are four.

¹Kramer, H.A., Proc. Amsterdam Acad. Sci. 33, 959 (1930).

D. Fuel Processing Facilities for EBR-II

1. Status of Construction

Construction of a fuel reprocessing-refabrication plant (Fuel Cycle Facility) for the direct recycle of fuel in the EBR-II reactor system was completed during 1962. This reactor will be the first demonstration of an integrated system operating on a closed fuel cycle; that is, the spent EBR-II fuel elements will be reprocessed, refabricated, and returned to the EBR-II reactor. The Fuel Cycle Facility will be used for the remote recovery of fertile and fissionable materials by pyrometallurgical methods and for the remote refabrication of fuel elements. The Fuel Cycle Facility will also be used as a pilot plant for the evaluation of new or improved pyrometallurgical recovery processes and fuel fabrication methods. Figure I-25 is an isometric sectional view of the Fuel Cycle Facility.

Figure I-25

ISOMETRIC SECTIONAL VIEW OF 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 reassembly of new subassemblies. A photograph of the inside of the Air Cell is shown in Figure I-26. The Argon Cell will be used for all operations which do 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. A portion of this cell is shown in Figure I-27. Processing operations in the Air Cell and the Argon Cell will be observed and controlled from operating areas outside the process cells. Service equipment which might periodically become radioactive will be located in the subcell area on the service floor. This area is beneath most of the Argon Cell and is separated from the service floor by a two-foot thick concrete wall.

Operations within the Air Cell and Argon Cell of the Fuel Cycle Facility are normally viewed through one of thirty-one windows installed in the five-foot thick, heavy concrete shielding walls. Each window consists of two remotely replaceable 9-inch thick glass panes on the hot side of the cells and an oil-filled tank unit containing four 9-inch thick glass panes. A seal is made with a 1-inch thick glass pane located between the tank unit and the replaceable glass panes. The windows will be protected by steel shutters when the windows are not in use, thereby lengthening the useful lifetime of the windows.

All shielding windows have been completely installed. The light transmittance through the 5-foot thick windows was determined to be from 15 to 17 percent. This considerably exceeds the specified light transmittance of 9 percent. General viewing and resolution quality are excellent.

The integrity and adequacy of the shielding of the Argon and Air Cells was determined by radiographing. Irradiated sodium (sodium-24) was used as a source of gamma radiation in the survey. The effectiveness of the shielding walls for attenuating gamma radiation was determined by locating the gamma sources on a three-foot grid pattern adjacent to the walls, and at floor and ceiling positions of interest and measuring any radiation which penetrated the shielding walls. About 11,000 sq ft of shielding surface of the Air and Argon Cells was surveyed in this manner. An analysis of the radiographic data indicated that the shielding is adequate. No evidence of major voids or leaks in the concrete was found. The data revealed that the radiation level at the outside of the five-foot-thick, heavy concrete shielding wall of the Argon Cell for the most radioactive cell operation will be less than one milliroentgen per hour.

Figure I-26

AIR CELL

The Air Cell will be used for the disassembly of spent fuel subassemblies and the reassembly of new subassemblies. A view inside the Air Cell looking away from the Argon Cell is shown in the photograph. In the upper right corner of the cell, an electromechanical manipulator trolley is seen being lifted through a floor opening in the Air Cell by a remotely operated five-ton crane. All transfers of large items to the process cells are made through this floor opening. In the upper left corner of the cell, the remote installation of a light fixture by means of an electromechanical manipulator is seen. Three 6-foot-diameter by 6-inch thick steel shielding slabs for the opening in the Air Cell floor are seen at the left rear corner of the cell. A steel shielding plug for the 24-inch diameter opening in the steel slabs may be seen in back of the shielding slabs. A yoke to be used in conjunction with a basket (not shown) for lifting equipment items weighing up to 10,000 pounds from the large transfer lock between the Air and Argon Cells is seen in the right foreground. Conduits rising above the floor near the walls will be used to provide services into the cell. The circular disks at near floor level in the center of the Air Cell cover ten-foot deep storage pits for fuel subassemblies and solid waste collection containers.

Figure I-27

A VIEW INSIDE THE ARGON CELL OF THE FUEL CYCLE FACILITY

The Argon Cell will be used for decanning fuel pins, purification of irradiated fuel, fabrication of new fuel pins, and assembly of fuel elements. The melt-refining furnace is shown with its bell jar cover in the "up" position. The installation of the furnace was carried out by remote means. In the right foreground, a bank of service feed throughs is seen at floor level. Shown (from left to right) are induction heating, vacuum, electrical and thermocouple, and pneumatic feed throughs. In the left foreground, a part of a manipulator tool rack and changer is shown. Manipulator and crane bridges span the work area. Two steel shielding 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. A single-type shielding shutter is on the left; a split-type shielding shutter is on the right.

Because of the highly reactive nature of the nuclear fuel materials and scrap fuel materials that 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 and less than 5 parts per million of water vapor. The potentially high concentration of volatile fission products in the Argon Cell atmosphere also necessitates that the cell be operated at a cell pressure which is lower than the pressure in the surrounding areas. Because of these two factors, the Argon Cell was designed and constructed to insure a low rate of air inleakage into it and was equipped with a purification system for removing oxygen and water vapor to very low concentrations in the argon atmosphere.

The rate of air inleakage into the Argon Cell has been determined by a sensitive leak test method which involves replacing the air in the Argon Cell with nitrogen and measuring the increase in oxygen content of the nitrogen in the cell. This method of testing has also provided valuable information concerning the procedures that will be necessary to replace the cell atmosphere with argon in the most economical manner. The oxygen level in the cell (cell volume of about 60,000 cu ft) was reduced to about one percent by a two-step addition of nitrogen. The total volume of nitrogen used was 160,000 cu ft. The oxygen level was then further reduced by operating the argon purification system. The results of leak tests, based on data obtained during various testing periods when the argon purification system was not in operation, indicated an air inleakage rate buildup of less than 0.006 cfm at a pressure in the Argon Cell of minus four inches of water. The design specification leak rate for the Argon Cell is 0.01 cfm at a cell pressure of minus two inches of water. The air inleakage determinations were made at oxygen levels in the Argon Cell of 8 to 30 ppm and at a water level of about 5 ppm. The results of this test indicate that the Argon Cell is, at present, adequately gas tight.

The argon purification system removes oxygen and water vapor from the Argon Cell atmosphere. The oxygen is removed by the catalytic reaction of oxygen with added hydrogen to form water vapor. The water vapor formed by the reaction and the water vapor present in the cell atmosphere before conversion of the oxygen to water vapor are then removed by a dessicant. The equipment items in the purification system include a compressor, a catalyst bed, and a dessicant bed.

Because the air-inleakage tests involved measuring the increase in oxygen level of the nitrogen in the cell, the purification system was not operated continuously. Furthermore, the rate of hydrogen feed to the cell gas stream ahead of the catalytic bed was maintained at less than the stoichiometric requirement necessary to react with all the oxygen passing through the purification system. Despite these restrictions, the concentration of oxygen in the cell was periodically reduced below

20 parts per million and occasionally below 10 parts per million (specification limit for oxygen: < 100 ppm). Tests showed the gas flow rate through the purification system to be 270 cu ft/min. With the cell gas flow rate of 270 cu ft/min through the purification system and the air-inleakage rate of 0.006 cu ft/min, it appears that a concentration of oxygen of less than 5 parts per million could have been attained in the Argon Cell with the addition of the stoichiometric requirement of hydrogen and with continuous operation of the purification system.

Although the Argon Cell must operate at a lower pressure than atmospheric, the large wall surfaces (72 feet in diameter by 22.5 feet high) require that the difference between the cell pressure and the pressure of the surrounding areas should not be excessive. The cooling system for the Argon Cell is capable of controlling the Argon Cell pressure between minus 2 and minus 6 inches of water. Cooling of either or both of two 15,000 cu ft/min circulating gas streams is done by a bank of cooling coils. The coolant flow to each bank of cooling coils is controlled by four freon control valves which are sequentially modulated as the demand varies. Since a change of one degree Centigrade in the average cell gas temperature causes 1.1 inches of water change in the cell pressure, the proper control of the coolant flow is imperative. During the seven-week period of the air-inleakage tests, the controls for the cooling system normally maintained the pressure in the Argon Cell within one-half inch of water of the controller set point.

2. Equipment for EBR-II Fuel Cycle Facility

All operations in the Air and Argon Cells of the Fuel Cycle Facility will be carried out by remote control and will be performed usually by means of cranes or electromechanical manipulators. The cranes and manipulators were designed to be very strong, dependable, and radiation stable, and to permit remote maintenance on most of the component parts of cell equipment. All the cranes and the manipulators for the Argon and Air Cells have been installed.

Process equipment was installed by remote means using the manipulators in order to assure that subsequent hot operations could be done remotely as well as to give the operators experience. Process equipment items which were assembled and installed by remote means included the melt refining furnaces, the ingot removal and handling device, the injection casting furnaces, a sodium settling furnace, and a sodium bonding machine.

Four wide-angle viewers have been installed in the roof and the walls of the Argon Cell to view the interior of the cell. Portable, variable-power spotting telescopes (up to 30X) have been modified for use with the wide angle viewers for inspecting the panoramic image in greater detail.

While most operations in the fuel reprocessing cycle will be conducted within about five feet of a shielding window, some cell maintenance operations will be accomplished by means of a manipulator at distances up to 18 feet from the window at which the operator of the manipulator is stationed. Since depth perception is one of the most troublesome problems in the use of remotely controlled manipulators in a large hot cell, stereo-optical depth perceptrs have been designed to overcome this problem.

The Argon Cell is a sixteen-sided polygon. The floor area in the cell is considered to consist of sixteen modules for purposes of process equipment location. Thirteen of these modules were each provided with a bank of five service sleeves. Electrical and other services are brought into the Argon Cell by means of removable feed-throughs installed and sealed in the service sleeves which penetrate the floor of the cell (see Figure I-27).

The feed-throughs and the sleeves have a stepped design which prevents radiation leakage. Each feed through can be remotely removed and replaced without affecting the integrity of the argon atmosphere in the Argon Cell.

Figure I-28
SMALL TRANSFER LOCK
BETWEEN AIR CELL
AND ARGON CELL

3. Transfer Lock System

All transfers of materials to the Air Cell and of materials intended for the Argon Cell will be made through an opening in the floor of the Air Cell (see Figure I-26). Transfer of materials between the Air Cell and the Argon Cell will be made through either of two small transfer locks (see Figure I-28) mounted horizontally in the shielding wall between the Air Cell and Argon Cell or through a large transfer lock (see Figure I-29) mounted vertically in the floor of the Argon Cell. The transfer locks maintain the integrity of the argon atmosphere in the Argon Cell while transfers of materials are being made.

The small transfer locks consist of two horizontal rectangular tubes which pass through the 4-ft shielding wall between the Air Cell

and the Argon Cell. Material is transferred in small carts which ride on rails mounted inside the locks. Direction of travel is determined by the slope of the rails, which can be changed remotely with the operating manipulator. Items 2 ft high and 1 ft in diameter may be transferred. Special end fittings, which allow loading and unloading of the carts, are bolted to each end of the locks. Hinged lids sealed by rubber gaskets are used to close the openings in the lock ends. In each case, the entire lock end is replaceable.

Figure I-29

LARGE TRANSFER LOCK IN ARGON CELL

The large transfer lock is basically a 6-ft-diameter cylinder, 8 ft long. It is composed of three major sections. The upper section consists of a spool piece with a counterbalanced hinged lid which is sealed by a lead or rubber gasket. This section is weld sealed to the middle section, which penetrates the 4-ft-thick cell floor. The bottom of the lock is a steel platform which can be elevated by a hydraulic ram and seals to the lower flange of the center lock section with a rubber J-ring gasket. The load capacity of the lift is 5 tons. The platform and ram are part of the Transfer Cell equipment on the service floor which moves material from an opening in the Air Cell floor to the large transfer lock. Other components of this equipment are the transfer cart, which carries the platform between the two loading points, and a second ram, which raises the platform into the Air Cell.

4. Interbuilding Transfer Coffins

EBR-II fuel subassemblies containing either spent or reconstituted fuel will be transferred between the Reactor Building and the Air Cell of the Fuel Cycle Facility in 20-ton interbuilding fuel transfer coffins. Two designs have been made and will be evaluated in service. Both designs provide for removal of fission product heat from the subassembly by means of a circulating stream of argon. In one design, the argon stream is cooled by passing it through an argon-to-air heat exchanger. This coffin, which was designed and fabricated by O. G. Kelley and Company of Boston, Massachusetts, has been delivered to the Fuel Cycle Facility where it is undergoing tests. In the other design, which was developed by the Chemical Engineering Division of Argonne National Laboratory, the heat from the circulating argon stream is transferred into the massive lead shielding of the coffin. This coffin is being fabricated at Argonne National Laboratory and will be completed during the summer of 1963.

5. Sodium Removal from Spent Fuel Subassemblies

When a spent EBR-II fuel subassembly is loaded into an interbuilding transfer coffin, the subassembly will be coated with a thin film of sodium. Because of its pyrophoricity, this coating of sodium must be removed before the subassembly is transferred from the coffin into the Air Cell at the Fuel Cycle Facility. To accomplish this, a sodium removal station has been designed. It is to be located in the passageway between the Reactor Building and the Fuel Cycle Facility. Waste-sampling and waste-disposal equipment are also being provided for this station.

The removal of sodium from a subassembly will be carried out while the subassembly is in the coffin. The sodium-removal process which will be used involves the conversion of the sodium to sodium hydroxide and the removal of the sodium hydroxide by means of a water wash. The chemical conversion is to occur in two steps. First, the sodium is to be converted to the oxide by the addition of a small flow of air to the recirculating coolant gas, with any pressure buildup relieved through a bleed to the suspect stack. In the second step, the oxide is to be converted to the hydroxide by the addition of humidified air. The sodium hydroxide film is to be removed by a once-through water wash, and the subassembly is to be dried by a flowing stream of air.

Calculations have been made in order to determine values of parameters for this sodium-removal procedure. The calculations, for which it was assumed that there will be a 100-g holdup of sodium in the subassembly, show that about 15 min must be allowed for each of the two steps in the sodium-to-sodium hydroxide conversion if an average chemical heat generation of one kilowatt is to be maintained. It is desirable to

limit the chemical heat load to about this value to prevent fuel pins in the subassembly from becoming excessively hot (greater than 600 F*). In practice, the reaction rate will be controlled by limiting the concentration of oxygen and water vapor added to the recirculating coolant gas while monitoring the temperature of the gas leaving the subassembly. The required addition rate for air will be about 0.4 cfm, and the addition rate for humidified air which has been 80 percent saturated at 70 F will be about 7 cfm. The water wash will be limited to about 25 gal, and the system will be designed to deliver about 5 gal/min.

Results of small-scale laboratory experiments indicate that the proposed sodium-removal process is satisfactory. Analysis of gas samples taken during the various steps indicated that no more than a trace of hydrogen was produced by the reactions. It is anticipated that further development of procedures will be necessary. When subassembly coffins become available, additional work is to be done at the EBR-II site with sodium-coated, unirradiated, full-scale subassemblies.

6. Radiation Stability Testing of Materials

The radiation levels inside the process cells of the Fuel Cycle Facility will be such that the dose to exposed items will range from ten million to ten billion rad per year, depending on their specific location. A concerted and continuing effort has been made at Argonne to determine the effect of such dosages upon construction materials and equipment components and to find a means whereby the useful life of such components can be extended. The current investigation has been concerned with the testing of elastomers for use as a gasket material.

Various elastomers have been tested to determine their suitability as a gasket material to replace the lead gasket specified for use on the large transfer lock in the Argon Cell. The elastomer samples, neoprene, gum rubber, and Adiprene C,** were irradiated while under compression in a test assembly which simulated the gasket surface of the large transfer lock. Both neoprene and gum rubber were permanently "set" in the test assembly following irradiation to 6×10^7 rad, but they were still resilient and judged serviceable. Further irradiation of the neoprene indicated it would be serviceable for use as a gasket material to about 2×10^8 rad, but it was judged too hard at 3.2×10^8 rad. The gum rubber was still resilient and considered possibly serviceable at 4×10^8 rad, but it exhibited loss of strength (it crumbled and was easily punctured) at 2×10^8 rad. Adiprene C was soft and resilient following irradiation to 1×10^9 rad and it was still sufficiently resilient after an exposure of 3×10^9 to be judged serviceable at this level of irradiation.

*This temperature (600 F) has been chosen as a design criterion.

**A product of Minnesota Rubber Company.

7. 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 certain noble fission product elements that 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 modifications, 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 skull material 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 material is transformed to a powder which is readily poured from the crucible. A furnace for the skull oxidation step has been constructed and tested at Argonne. Associated with the furnace is an oxygen feed-control system which regulates the rate of the oxidation reaction. In experiments with oxygen as the oxidant, the results show that the oxygen consumption rate was equivalent to a conversion rate of one to two grams of uranium per minute. The oxidation reactions proceeded smoothly and resulted in complete oxidation of the skull material. The oxide product was found to be free of undesirable agglomerates.

A plant-scale skull oxide-processing furnace which will be used to study the steps of the skull reclamation process which follow skull oxidation has been built, and preliminary tests have begun. High frequency (10 kilocycle) heating and mechanical mixing will be used in the initial tests. The prototype furnace will be capable of handling 5 kilograms of skull oxide.

In separate experiments, the use of low frequency (60 cycle) inductive heating and mixing is being investigated. Appreciable simplification of equipment for the skull reclamation process would be possible if this method is feasible. Experiments have been performed with zinc, magnesium, and zinc-salt flux mixtures. Various induction coils have been tested to determine the optimum coil configurations. The determination of the degree of mixing has been limited to observations of the agitation at the surface of melt, but these observations indicate that low frequency inductive agitation is vigorous.

Heating with low-frequency inductive power was also satisfactorily demonstrated in experiments in which zinc and zinc-salt flux mixtures were heated to 800 C, the operating temperature of the skull reclamation process. The use of a low-frequency (60 cycle) supply system appears promising for providing the necessary power for heating and mixing of plant-scale charges in the skull reclamation process. The installation of larger power-supply equipment (37 kw) for engineering-scale studies is complete. Further work is planned with this larger power-supply system.

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. Equipment for this step of the reclamation process is being developed and tested.

Methods for collecting the magnesium-zinc vapors evolved in the distillation are being investigated. For remote operation, the component parts of the apparatus must be capable of being readily assembled and, after distillation of the magnesium-zinc, of being easily disassembled from each other. A condenser and collector design (see Figure I-30) is being evaluated in which the condensed magnesium-zinc vapors are collected in a collector positioned above the crucible. The collector will be discarded after each run. The condenser and furnace crucible, however, will be used for more than one run. The component parts were fabricated of type CS graphite. The results of runs with collectors of four different shapes indicated that the shape of the bottom of the collector was important for the distillation of the final trace amounts of magnesium-zinc alloy from the furnace crucible and for preventing the formation of a magnesium-zinc bond between the collector and the furnace crucible, which would make their separation by remote handling difficult.

Two runs were made in which the component parts of the apparatus were fabricated of a more impervious grade of graphite (ATJ) than the graphite (CS) used in runs discussed above. In each run, 1000 grams of 50 weight percent magnesium-zinc was charged to the

crucible. In the two runs, 99.5 percent of the magnesium-zinc charge was distilled. In the first run, 92.8 percent of the distillate was collected in the collector, 2.2 percent was collected in the condenser, 2.2 percent was collected on the Fiberfrax* insulator, and 2.8 percent was unaccounted for.

Figure I-30

DISTILLATION APPARATUS FOR THE REMOVAL
OF RESIDUAL MAGNESIUM-ZINC FROM
URANIUM PRECIPITATES

In the second run, 91.2 percent of the distillate was collected in the collector, 5.1 percent was collected on the Fiberfrax insulator, and 3.7 percent was unaccounted for. No magnesium-zinc was found in the condenser. A comparison of the results of these tests with previous tests shows that some improvement was obtained by using the more impervious grade of graphite. With ATJ graphite, a greater amount of magnesium-zinc was collected in the collector (91 to 93 percent as compared with 85 percent for the CS graphite) and a lesser amount was found on the Fiberfrax insulator (2 to 5 percent as compared with 8 percent for the CS graphite).

This condenser and collector design shows considerable promise as a method for collecting the condensed magnesium-zinc vapors evolved in the distillation step. Additional experiments are planned to test modifications in the design which would

minimize the possibility of equipment components being bonded to each other after a distillation run since such bonding would hinder remote disassembly of the equipment. Also, in future distillation experiments, the more impervious ATJ graphite will be used for the fabrication of the condenser and the collector.

*An alumina silicate type of insulation manufactured by the Carborundum Company.

II. VOLATILITY AND FLUIDIZATION PROCESSES

A. Fluoride Volatility Process Development

Interest in the fluoride volatility processes has increased recently both in this country and in Europe, largely because of improvements in process concepts and advances in process development. In these processes, uranium and plutonium in spent nuclear fuels are converted into hexafluoride compounds which are volatile and can therefore be separated from fission product elements and from cladding and alloying materials by comparatively simple techniques such as vaporization and distillation. Fluoride volatility processes are the only promising alternatives to the existing aqueous solvent extraction processes which are capable of high decontamination (such that direct handling procedures can be used in some cases during fuel element refabrication). These nonaqueous processes offer a large number of advantages over the solvent extraction processes and show excellent promise for reducing the cost of nuclear fuel reprocessing in the future. Some of these advantages are the following: (1) ease of separation of uranium hexafluoride from impurities, (2) the use of reagents with low susceptibilities to deleterious radiation effects, (3) virtual absence of neutron moderating chemicals in the process, (4) a uranium product (uranium hexafluoride) in the form desired for isotope separation, (5) a plutonium product (plutonium hexafluoride) in a form suitable for direct conversion to metal or oxide, and (6) radioactive waste products in a solid form.

The two most significant recent advances in fluoride volatility process technology are: (1) the demonstrated ability to prepare, handle, and store plutonium hexafluoride with safety and without appreciable nonrecoverable losses, and (2) the application of fluidized-bed techniques for conducting direct chemical conversion of fuel materials into gaseous compounds. The result of these developments is that it now appears possible, for many types of nuclear fuels, to employ gas phase reactions in a controllable manner, to remove the cladding or alloying metals by volatilization, and to convert the fissionable materials to readily separable volatile compounds.

Processes are under development for application to a variety of nuclear fuels of both the low-enrichment type commonly used in central station power reactors and the high-enrichment type used in mobile power reactors, test reactors, seed-and-blanket reactors, and others.

1. Processing of Nuclear Reactor Fuel of Low Enrichment

The type of nuclear fuel currently contemplated for most central station power reactors consists of compacted uranium dioxide in tubes of either Zircaloy or stainless steel. The uranium is of low enrichment (below 5%), and after irradiation the fuel will contain a small percentage of plutonium which must be recovered with the uranium.

The conceptual flowsheet for the reprocessing of fuels of this type involves the following major steps: (1) separation of uranium and plutonium from the fuel jacket, (2) fluorination of the exposed fuel with fluorine gas at elevated temperatures, followed by condensation of the mixed hexafluorides of uranium and plutonium, (3) distillation to remove fission products and to partition the hexafluorides into uranium hexafluoride and a concentrated mixture of plutonium hexafluoride and uranium hexafluoride, and (4) separation of plutonium from uranium by thermal decomposition of PuF_6 .

Engineering-scale process development work has been concentrated largely on two important aspects: first, investigation and demonstration of the fluorination of unirradiated uranium dioxide on a practical scale; and second, design and construction of a pilot facility to permit development of the individual process steps using simulated fuel containing both uranium and plutonium. The latter program requires a special facility of the glovebox-type to permit work with the highly radiotoxic plutonium.

a. Engineering-Scale Fluorination of Unirradiated Uranium Dioxide

The fluorination of nonirradiated, sintered pellets of uranium dioxide, a form commonly used in fuel elements, was continued in pilot-scale equipment to study further the reaction conditions most suitable for plant application of this fuel recovery process. The experiments were carried out in a three-inch diameter, air-cooled nickel reactor. Alundum (grains of aluminum oxide) was used in the void spaces of the static bed of uranium dioxide pellets and, on being fluidized, was highly beneficial in aiding heat transfer and maintaining isothermal conditions. Early in the work on the fluorination of uranium dioxide pellets by fluorine gas, it was found that the reaction could be carried out in a controlled manner under certain conditions of operation. However, in later work complications arose when the excess fluorine gas was recycled in order to achieve more efficient utilization of the fluorine reagent. Since the recycle gas contained oxygen (a product of the reaction of uranium dioxide with fluorine), the uranium dioxide pellets were in part converted to U_3O_8 powder before fluorination. This had the beneficial effect of increasing the surface area of the uranium oxide, thus promoting more rapid fluorination. However, at high ratios of oxygen to fluorine, excessive formation of U_3O_8 fines occurred, which offset the advantage of fines formation by causing cakes to form in the bed in some runs.

In batch runs, the depth of the UO_2 pellet bed was also found to be an important variable. In deep beds (18-inch uranium dioxide pellet bed depth), caking occurred more readily than in shallower beds. Caking appeared to result from poor fluidization and from chemical interaction of uranium oxides and fluorides producing sinterable reaction products. In the 18-inch deep beds, satisfactory fluorination was achieved at 500 C at rates of about 35 lb UF_6 /(hr)(sq ft of reactor cross section) with

fluorine utilization efficiencies of about 30 percent. Higher fluorine efficiencies could be achieved, but only at lower fluorination rates.

In an effort to optimize the fluorination operation, alternative procedures were investigated. Successful fluorinations of six-inch deep beds were carried out continuously by feeding uranium dioxide pellets to the reactor during fluorination to maintain a constant inventory of uranium holdup in the reactor. During 20 hours of operation at 500 C, rates of up to 40 lb $\text{UF}_6/(\text{hr})(\text{sq ft of reactor cross section})$ were obtained, with fluorine efficiencies ranging from 56 to 76 percent. A significant result of this continuous pellet-bed run was the fact that the great variation of sizes of the fixed, random-packed bed of uranium dioxide pellet fragments which resulted from the continuous mode of operation apparently did not interfere with overall operability. This fragmented state of pellets probably corresponds more closely than whole pellets to actual reactor fuel material.

Recent emphasis has been placed on a two-zone, oxidation-fluorination scheme in order to achieve improved performance, without caking, for the batch processing of deeper pellet beds. In this scheme, the lower zone consists of a static bed of UO_2 pellets with fluidized Alundum grain in the voids between the pellets; the upper zone consists of a fluidized

Figure II-1
SCHEMATIC DIAGRAM
OF FLUORINATOR IN
TWO-ZONE OPERATION

bed of Alundum grain which extends above the bed of uranium dioxide pellets. An oxygen-nitrogen gas mixture is introduced as fluidizing gas into the bottom of the 3-inch diameter reactor, and fluorine is introduced just above the pellet bed. Uranium oxide fines (U_3O_8) are formed in the lower zone and transported into the upper zone, where they are fluorinated to form uranium hexafluoride vapor which leaves the reactor as a component of the gas stream. A schematic diagram of the fluorinator used in the two-zone experiments is shown in Figure II-1.

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 ($\Delta H = -26 \text{ kcal/gram mole uranium at } 25 \text{ C}$)

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.

Initial two-zone runs, made with 12-inch deep pellet beds (lower zone) and a 24-inch upper fluidized zone, exhibited a virtual absence of caking tendencies. Complete fluorinations in as short a time as 14 hours have been obtained, with overall average fluorine efficiencies of about 50 percent. Uranium hexafluoride rates of 100 lb UF_6 /(hr)(sq ft) and fluorine efficiencies of 80 percent have been obtained during some periods of operations. In these runs, upper-zone temperatures have been 500 C. In the lower zone, the variables of temperature and oxygen concentration are being investigated for control of the rate of oxidation.

Experiments are planned to extend fluid-bed oxidation studies to the separation of uranium oxide fuel from cladding in typical fuel elements. Such a process step is an alternative to chemical decladding of Zircaloy and stainless steel. This method entails mechanical broaching of the cladding by shearing or perforation so that oxidative pulverization of the uranium dioxide can occur. The uranium oxide fines produced in this oxidation zone will be conducted to a fluid-bed fluorination zone, as outlined above. The cladding is expected to be unreacted and will be removed mechanically.

Supporting studies have been made of the basic behavior of fluidized-packed beds for the purpose of assisting in the design and interpretation of process equipment operation. Previously, heat transfer studies in mock-up systems had established typical values of fluid bed-to-wall heat transfer coefficients and of effective thermal conductivities in the radial direction. These typical values were, respectively, 40 Btu/(hr)(sq ft)(F) and 10 Btu/(hr)(sq ft) (F/ft) under conditions that correspond to conditions in the fluid bed fluorination of uranium dioxide pellets. Preliminary measurements of effective axial thermal conductivity in fluidized-packed beds of configuration similar to those used for fluorinations have now been made. These axial coefficients are higher than the radial coefficients by a factor of 10 or more; values of effective axial thermal conductivity of up to 600 Btu/(hr) (sq ft)(F/ft) were observed. Studies of gas mixing and solids mixing in fluidized-packed beds have also been made to support the process development. It was found that gas eddy diffusivities in the radial direction for beds of fixed packing had approximately the same values when solids were fluidized in the voids of the packing as in the corresponding case without the fluidized material. A study is in progress on mixing of solids fluidized in the voids of a fixed bed of packing. It has been found that solids mixing rates in the radial direction can be characterized by a diffusion constant. On the basis of this preliminary work, fluidized solids diffusivity in packed beds of spheres has been correlated with gas velocity, packing size, and fluidized particle size.

b. Engineering-Scale Plutonium-Handling Facility for Fluoride Volatility Studies

An engineering-scale, high-alpha facility is being constructed to study various steps of the fluoride volatility processes for the recovery of uranium and plutonium from nuclear fuels. A schematic flow diagram of the engineering-scale equipment being installed for development of this process is shown in Figure II-2. The major process steps include fluorination of the fuel, condensation of the hexafluoride products, distillation, and final separation of plutonium product by means of thermal decomposition. As an alternative step of the cycle, it is also planned to study the direct conversion of mixed uranium and plutonium hexafluorides to dioxide in a fluid-bed reactor to be installed in the same facility.

Figure II-2

FLOW DIAGRAM OF PILOT PLANT EQUIPMENT.
DIRECT FLUORINATION PROCESS

The process equipment is housed in two large alpha-containment boxes of a modular type designed by the Chemical Engineering Division. One of the boxes is the largest of this type built to date.

Neoprene gloves will allow access to the equipment from both sides of the boxes. A unique feature is large, 30-inch diameter, bag-out ports on the top of the box to allow removal and installation of large pieces of equipment. The behavior of fission products can be investigated in this system at gamma levels that allow direct personnel access. A scale model of the large box with part of the equipment installed is shown in Figure II-3. The model was constructed to facilitate the layout of equipment and service lines.

As of April 30, 1963, the installation of the facility and the initial process equipment was 70 percent complete. Present schedules indicate that facility construction will be virtually complete by the end of 1963, and that after preliminary testing without plutonium, plutonium operations may begin in early 1964.

2. Processing of Nuclear Reactor Fuel of High Enrichment

The high-enrichment nuclear fuels are of several types. The most important type at the present time is fully enriched uranium alloyed and clad with either aluminum or Zircaloy-2.* Process development studies have been directed principally toward the zirconium-based alloy fuels, but preliminary work has indicated that the process is equally applicable to the aluminum-based alloy fuels. Since the spent fuels contain only negligible amounts of plutonium, the recovery process is intended for uranium only and the plutonium is discarded with the fission products.

The conceptual flowsheet (Figure II-4) for the recovery of uranium from these alloy fuels employs two principal steps, in which chemical separation of the various fuel constituents is achieved by selective volatilization of chlorides and fluorides. Fluidization techniques are employed in the volatility process, since fluidized beds offer the means of conducting and controlling highly exothermic reactions under nearly isothermal conditions. The initial process step involves the reaction of the alloy with hydrogen chloride gas while the fuel elements or assemblies are submerged in an inert fluidized bed of Alundum particles. This reaction is conducted at temperatures above the sublimation point of the alloying metal chloride (331 C at 1 atm for zirconium tetrachloride), thus providing the means for separating the bulk of the alloying metal from the uranium. The uranium is converted to solid uranium trichloride during hydrochlorination. The uranium trichloride remains, for the most part, in the fluid-bed zone of the reaction column. However, a portion of it is entrained in the off-gas and in order to insure adequate uranium retention within the system, as in most other systems, it has been found necessary to employ a high-temperature gas filter in series with the fluidized-bed reactor. Packed-bed filters were tested. Filters which consisted of

*Zircaloy-2 is a high-zirconium alloy which contains, in addition to zirconium, 1.5% tin, 0.15% iron, 0.10% chromium, and 0.05% nickel.

Figure II-3

DIRECT FLUORINATION PROCESS SCALE MODEL OF PILOT- PLANT EQUIPMENT IN PLUTONIUM HANDLING FACILITY

DIRECT FLUORINATION PROCESS
SCALE MODEL OF PILOT PLANT EQUIPMENT IN PLUTONIUM ENCLOSURE

Figure II-4

SCHEMATIC FLOWSHEET OF URANIUM ALLOY FUEL PROCESSING PILOT PLANT

alternate layers of coarse and fine Alundum particles or of coarse particles alone were effective in removing particulate material from the hydrochlorination off-gas stream. Recovery of uranium as volatile uranium hexafluoride is achieved in the second step of the process by reaction of uranium trichloride with fluorine. The uranium hexafluoride product is collected by cold trapping.

Bench-scale engineering tests on these process steps have been conducted in a $1\frac{1}{2}$ -in. diameter fluidized-bed reactor. These tests were evaluated primarily on the basis of the percentage of the uranium feed recovered as uranium hexafluoride and the distribution of unrecoverable uranium values. The overall objective of these tests was to develop a processing procedure which would achieve a uranium recovery of at least 99 percent. Alloy charges consisting of approximately 240 g of five weight percent uranium-Zircaloy-2 chips have been completely reacted with hydrogen chloride in fluidized Alundum beds in five to six hours at a bed temperature of 400 C. Retention of uranium trichloride particulate matter (entrained by the volatile zirconium tetrachloride off-gas) has been successfully achieved by the use of a static bed of granular Alundum as a

high-temperature filter. Uranium losses from the system by transport through the filter have been consistently less than 0.2 percent.

A method was developed for the continuous analysis, by means of thermal conductivity cells, of the reaction product, hydrogen, in the filtered off-gas stream. During the hydrochlorination step, these cells furnished accurate data on the rate and progress of the reaction and on the efficiency of hydrogen chloride utilization. The method promises to have utility for automatic control of the reaction in plant-scale process applications.

Recovery of uranium as uranium hexafluoride in yields of approximately 99 percent has been consistently demonstrated by a two-step fluorination procedure. The fluorination conditions have been established as: two hours of exposure to flowing fluorine gas at 250 C, followed by an additional two hours of exposure at 500 C. Results from several tests have shown that reuse of the fluid-bed and filter-bed material is possible without affecting the recovery of uranium in subsequent runs. Thus, it should be possible to allow the radioactive waste products to accumulate to a high concentration in the Alundum bed before the bed is removed for storage. Other chlorinating agents, such as phosgene and chlorine, and alternative reaction sequences have been evaluated in several exploratory tests, but no advantages were gained with respect to uranium recovery.

The volatile zirconium tetrachloride produced during hydrochlorination of uranium-zirconium alloy fuel represents a waste stream which will require processing for more convenient storage. Studies performed in a six-inch diameter fluid-bed reactor have shown that zirconium tetrachloride may be converted readily to solid zirconium dioxide by gas-phase reaction with steam. A gas stream consisting of zirconium tetrachloride and nitrogen was fed directly into a heated (350 C) bed of zirconium dioxide. Steam was supplied to the fluidized bed through a separate inlet tube. Satisfactory results have been obtained in tests with zirconium tetrachloride feed rates up to 5 kg/hr. Although a large portion of the zirconium dioxide is produced in the form of fine particles (minus 200 mesh), operation of the fluid-bed column has been trouble-free in runs of up to 12-hour duration. The sintered metal filters used on the off-gas stream have shown no tendency to plug, and the use of a blowback procedure for cleaning the filters has successfully prevented buildup of dust cakes in the filters. Materials such as sand and refractory aluminum oxide have been found suitable for starting beds.

Because of the encouraging results achieved in the experimental work on zirconium alloy fuel, a pilot-scale facility has been designed and is being constructed in which up to 30 kg of fuel alloy may be processed in a single batch. A schematic drawing of the facility is shown in Figure II-4.

The hydrochlorination and fluorination reactions are carried out in a six-inch diameter nickel reactor. A fixed-bed down-flow filter in series with the fluid-bed reactor is incorporated to insure retention of uranium trichloride particulate solids. Zirconium tetrachloride produced during the hydrochlorination step is converted to zirconium dioxide by reaction with steam in a six-inch diameter stainless steel reactor. Off-gases from this unit are passed through a series of scrubbers and condensers before being exhausted from the building. Uranium hexafluoride, produced by fluorination of the trichloride, is collected in a system of refrigerated condensers. The fluorine gas stream is recycled through a remote-head diaphragm compressor, while a small quantity of the gas is bled to an activated alumina trap for fluorine disposal. The pilot-scale facility is fully instrumented, and many of the operations will be controlled automatically. The construction of this facility, which will be operated to demonstrate each of the process steps on a practical scale with unirradiated material, has been completed. Leak testing and shakedown tests are now being made.

Separate tests using irradiated feed and tracer techniques are planned for a bench-scale facility ($1\frac{1}{2}$ -inch diameter reactor) to be erected in the senior cave. The purpose of these tests will be to define clearly the disposition of fission products in the process and the decontamination achieved in each process step.

3. Preparation of Dense Uranium Dioxide Particles: Conversion of Uranium Hexafluoride to Uranium Dioxide by Fluid-Bed Techniques

A continuous, low cost process for the preparation of dense, spheroidal particles of uranium dioxide for use in swaged or vibratory-compacted nuclear fuel elements is under development. In this process, uranium hexafluoride is directly converted in a fluidized bed to uranium dioxide particles which are then sintered in hydrogen. Uranium dioxide particles having densities of up to 96.5 percent of theoretical density* have been produced by this method. Densities above 95 percent are considered, by fuel fabricators, to be suitable for the preparation of compacted fuel elements. The process offers considerable simplification over the costly series of batch steps now employed for conversion of uranium hexafluoride to dioxide and promises to eliminate the need for pelletization or arc-fusion of the uranium dioxide as a means of densification. Dense, spheroidal particles of this type may also have special applications in certain fuels, such as graphite-dispersion fuels for gas-cooled reactors.

*Theoretical density is 10.96 g/cc.

In earlier work under this program, a two-step fluid-bed process was developed for the conversion of uranium hexafluoride to uranium dioxide. This scheme gave particles which had a density of approximately 6 g/cc. Tests showed this product to be suitable for the preparation of pressed and sintered pellets, a form commonly used in power-reactor fuel elements. The "two-step" work has been successfully completed and reported in a topical report (ANL-6606). The current work involves a modification of the earlier process with the objective of producing a dense material suitable for use in compacted fuel elements.

The process under development for the direct conversion of uranium hexafluoride to uranium dioxide employs the feeding of steam and hydrogen simultaneously with uranium hexafluoride into a fluidized bed of uranium dioxide particles maintained at 650 to 700 C. Conversion of the hexafluoride to a dense solid is rapid and complete, the solid being deposited in layers on the surface of the bed particles. Figure II-5 shows the smooth, spheroidal appearance of the particles as produced in the fluid-bed, and Figure II-6 shows cross sections of a number of particles and illustrates the uniform manner in which the layers are deposited. Product of low residual fluoride content (300 ppm) was produced by alternating (at 30-minute intervals) periods in which uranium hexafluoride was fed and periods in which it was not fed, the steam and hydrogen flow being maintained constant. Control of the bed particle size was achieved by grinding and recycling to the bed a portion of the uranium dioxide product.

Figure II-5
DENSE URANIUM DI-
OXIDE PARTICLES AS
PRODUCED IN THE
FLUID-BED REACTOR

Final Particle Density,
9.3 g/cc

Figure II-6

CROSS SECTION OF DENSE URANIUM DIOXIDE
PARTICLES SHOWING LAYER DEPOSITION

1 mm

Etched 60 sec with
One part Conc H_2SO_4 ,
Nine Parts 30% H_2O_2

Uranium dioxide particles with densities, as determined by mercury displacement measurements, ranging from 8.5 to 9.5 g/cc (78 to 87 percent of theoretical density) were produced in runs at 650 C. In a run at a higher temperature, 700 C, particles with a density of 9.8 g/cc (89 percent of theoretical density) were produced.

Studies made at production rates of 45 lb uranium/(hr)(sq ft of reactor cross section) showed a dependence of particle density on steam concentration, higher densities being achieved with steam concentrations near the stoichiometric requirement (i.e., two moles steam per mole uranium hexafluoride).

The density of the uranium dioxide particles was increased by sintering in hydrogen for about $2\frac{1}{2}$ hours at 1600 to 1725 C. Final particle densities of 95 to 96.5 percent of theoretical density were achieved in tests on particles with starting densities of 78 to 89 percent of theoretical density. Also, the residual fluoride content of the particles was reduced from about 300 ppm to 5 ppm fluoride during the sintering step. Evaluation of this material for the preparation of vibratory-compacted fuel elements is planned by the Metallurgy Division as soon as the necessary compaction equipment is installed.

B. Laboratory Investigations of Fluoride Volatility Processes

Laboratory experiments were continued in support of the program for the development of fluoride volatility methods for the recovery and purification of nuclear reactor fuels. Studies were made to devise a fluorination scheme whereby optimum removals of uranium and plutonium could be achieved from the inert solids which will be used as fluid-bed materials and which will be discarded as waste after use. Experimental work was also continued on the separation of plutonium hexafluoride from uranium hexafluoride by thermal decomposition of the plutonium hexafluoride to the nonvolatile tetrafluoride at about 300 C. An adjunctive study to determine the behavior of uranium hexafluoride at this temperature was also carried out. The vapor phase hydrolysis of plutonium hexafluoride and the efficiency of filtration by AEC-type filters of the plutonium particulate matter resulting from the hydrolysis were subjects of additional investigations. Studies of the effect of gamma and alpha radiation on plutonium hexafluoride and the study of the gamma radiation-induced reaction of uranium tetrafluoride with fluorine were continued. Studies of a number of other reactions were carried out; these included (1) the reaction of uranium hexafluoride with hydrogen sulfide, (2) the reaction of plutonium compounds with fission product element compounds and (3) the reaction of mercury with plutonium hexafluoride. The absorption spectrum of gaseous plutonium hexafluoride was determined.

1. Removal of Plutonium and Uranium from Inert Solids

Since the inert solids that are used as fluidizing materials in the fluoride volatility processes are to be discarded as waste after use, it is economically important that methods for the optimum removal of plutonium and uranium from the inert solids be developed. The removal of these elements by a fluorination scheme has been studied. The studies were made in static systems in which small samples (2.5 to 3.0 g) of uranium-plutonium dioxides were mixed with fission product oxides and inert solids to simulate the mixtures that are likely to be encountered in plant processing. It is expected that a typical process charge will contain 100 kg uranium, 0.4 kg plutonium, and about 30 kg Alundum. About one kg of fission products will be present in 100 kg of uranium.

In one of the methods studied, the removal of uranium and plutonium from the inert solid material (Alundum) was accomplished by direct fluorination of the dioxides of the two elements. During the initial period of fluorination, in which most of the uranium is removed from the solid mixture, a low temperature (450 C) and a low concentration of fluorine (10 volume percent) were found to be desirable. However, to obtain satisfactory removals of plutonium in the last portion of the fluorination period, it was necessary to use a higher temperature (550 C) and a higher fluorine content (75 volume percent) in the fluorinating gas mixture. Plutonium removals of about 98.6 percent were achieved by this method.

A second method, in which a two-step procedure is employed, was also studied. In the first step, the uranium-plutonium dioxides were treated at 450 C with an oxygen-nitrogen gas mixture in which the concentration of oxygen was 20 volume percent. In this step the uranium dioxide is converted to uranous oxide. In the second step, the oxide mixture consisting of plutonium dioxide in uranous oxide was fluorinated using the same fluorination scheme employed in the direct fluorination method, i.e., a fluorination period at 450 C using 10 volume percent fluorine followed by a fluorination period at 550 C using 75 volume percent fluorine. This oxidation-fluorination procedure resulted in plutonium removals of 99 percent or greater (see Table II-1).

Table II-1

TWO-STEP FLUORINATION OF OXIDIZED URANIUM DIOXIDE-
PLUTONIUM DIOXIDE MIXED WITH ALUNDUM

Reaction Conditions

Oxidation: 450 C; 3 hr; 20 v/o O₂, 80 v/o N₂
 Fluorination: 450 C; 10 hr; 10 v/o F₂, 25 v/o O₂, 65 v/o N₂
 550 C; 10 hr; 75 v/o F₂, 25 v/o O₂
 Gas Flow Rate: 800 ml/min (linear velocity of gas, 5 ft./sec)
 System Pressure: one atm

Exp No.	(U-Pu)O ₂ ^a Batch No.	Initial Sample			Residue			Percent of Original Pu Removed
		Wt (U-Pu)O ₂ (g)	Wt Pu (mg)	Wt Al ₂ O ₃ ^b (g)	Wt (g)	Pu (w/o)	Wt Pu (mg)	
171	IV	2.830	8.17	0.850	0.900	0.006	0.05	99.4
172 ^c	IV	2.915	9.45	0.870	0.895	0.008	0.07	99.3
173	IV	2.795	9.08	0.840	0.895	0.007	0.06	99.3
174	V	3.420	10.9	0.900	0.855	0.009	0.08	99.3
175	IV	3.280	10.6	0.865	0.945	0.006	0.06	99.4
176	IV	2.905	9.45	0.870	0.915	0.006	0.05	99.5
177 ^d	IV	2.790	9.07	0.825	0.830	0.003	0.02	99.8

^a(1)(U-Pu)O₂ Batch IV. In the form of 1/4-in. by 1/4-in. pellets. Original mixture prepared by the addition of UO₂ and FP III mixture (see footnote (a) Table II-2) to a (U-Pu)O₂ mixture containing about four weight percent Pu. One gram of Batch IV contains 3.25 mg Pu, 890 mg U, and about 10 mg of fission product elements. (2) (U-Pu)O₂ Batch V. Prepared by the coprecipitation of ammonium diuranate and plutonium hydroxide followed by reduction at 1000 C to form a solid solution of PuO₂ in UO₂. To this solid solution, a mixture of ten fission product element oxides, designated FP III, was added (FP III contains BaO, ZrO₂, La₂O₃, CeO₂, Y₂O₃, Nd₂O₃, Sm₂O₃, Pr₆O₁₁, Eu₂O₃, and Gd₂O₃). One gram of Batch V contains 3.2 mg Pu, 867 mg U, and about 10 mg of fission product elements.

^bNorton's Blue Label Alundum - impurities: Not more than 0.01% of each of the following elements, Fe, Mg, Na, Si, Ti, Zr.

^cFluorination conditions

1st period 450 C; 15 hr; 10 v/o F₂, 25 v/o O₂, 65 v/o N₂

2nd period 550 C; 5 hr; 75 v/o F₂, 25 v/o O₂

^dThe 60 mesh Alundum used in this experiment contained 0.26 percent Fe, 0.35 percent Ni, and 0.33 percent Cr as chlorides which were formed during the chlorination of stainless steel.

2. "Decladding" and Recovery of Spent Oxide Fuels

In the conceptual flowsheet of the Direct Fluorination Volatility Process, the uranium and plutonium in spent oxide fuels will be recovered by fluorination of the oxides to produce the volatile hexafluorides. One of the "decladding" schemes which is being considered for this process employs an oxidation step for the removal of the uranium and plutonium dioxides from the cladding as a mixture of plutonium dioxide in uranosic oxide. In a study of this process step, it was found that oxidation of uranium dioxide at 450 C using air produced a finely divided powder of uranosic oxide. The product is in a form that is well suited to the fluorination step of the process.

Two schemes have been proposed for carrying out these reactions. In the first scheme, the oxidation and fluorination steps are carried out in the same fluid bed reactor; the oxidation step is carried out in the lower section of the fluid bed and the elutriated U_3O_8 powder is fluorinated in the upper section of the fluid bed. This scheme has been successfully demonstrated by the Fluidization and Volatility Engineering Group in experiments with uranium dioxide. In the second scheme, the oxidation is carried out in a separate reactor and the oxide powder formed therein is fed into a fluid bed of a fluorination reactor by gas transport in the nitrogen stream used to fluidize the bed.

The laboratory work has been concerned with the second of these operating schemes. Studies of the fluorination of uranosic oxide were undertaken to obtain data for the development of procedure and apparatus before starting work with materials containing plutonium. A $1\frac{1}{2}$ -in. fluid bed reactor was employed in the fluorination studies.

Work was completed on the development of methods for the feeding of uranosic oxide powder into the fluid bed and for the subsequent fluorination of the powder. This work resulted in the construction of a vibratory powder feeder which delivers the uranosic oxide powder at a constant rate to the fluidizing gas stream which then carries the powder into the fluid bed. The operation of the fluid bed reactor at 500 C with a feed rate of about three grams of oxide per minute and with 20 volume percent fluorine in a total gas flow of 12 liters per minute has resulted in conversion of about 98 percent of the uranosic oxide to uranium hexafluoride.

Further study has resulted in the addition of an automatic blowback arrangement to the apparatus, improvement in the cold-trapping efficiency, and the use of recycled fluorine for reaction with residual uranosic oxide. Preliminary experiments using a revised fluid bed fluorination system with a recycle period of five hours and using 100 percent fluorine as the gas phase indicate that an ultimate conversion of more than 99.5 percent of the uranosic oxide to the hexafluoride can be obtained.

A $1\frac{1}{2}$ -in. fluid bed reactor has been installed in an alpha box for operation with plutonium. The fluid bed fluorination of plutonium-bearing uranosic oxide will be carried out to demonstrate the feasibility of this operation and to obtain material balances for both uranium and plutonium. This apparatus will allow many experiments to be performed with smaller quantities of costly simulated fuel materials than are needed for runs in the pilot plant.

3. Separation of Plutonium Hexafluoride from Uranium Hexafluoride by Thermal Decomposition

In processing oxide fuels by the Direct Fluorination Process, a mixture of uranium and plutonium hexafluorides will be evolved from the reaction vessel in the fluorination step. It will be necessary to separate the mixture and to recover the components in pure form. Studies have been continued on the thermal decomposition of plutonium hexafluoride to form nonvolatile plutonium tetrafluoride as a means of accomplishing the separation. Efficient removal of plutonium from a flowing gas stream of uranium hexafluoride and plutonium hexafluoride was obtained by decomposing plutonium hexafluoride on a surface of plutonium tetrafluoride contained in a reactor at 150, 200 and 300 C. The data are given in Table II-2.

Table II 2
SEPARATION OF GASEOUS MIXTURES OF URANIUM HEXAFLUORIDE AND
PLUTONIUM HEXAFLUORIDE BY THERMAL DECOMPOSITION

Mixtures of UF_6 (~90 mm Hg) PuF_6 (~10 mm Hg) and He (~600 mm Hg) were circulated through nickel vessels packed with nickel wool

Volume of each packed vessel 100 ml
Volume of total system 9300 ml

Temp of Decomp Vessel (C)	Total Internal Geometric Surf Area (sq cm)	Wt PuF_6 Initially in Vessel (g)	Circulation ^a Time (hr)	Analysis of Gas Sample			Percentage ^b of Initial Pu Removed from Gas	Analysis of Solids Deposited from Gas Mixture		
				Wt U (mg)	Wt Pu (mg)	Ratio (U/Pu)		Vt U (g)	Wt PuF_6 (g)	Percent U in Solid ^d
150	1.6×10^3	3.891	0	34.9	3.3	10.6				
			1-1/4	45.1	3.96	11.4	6			
			5	37.6	2.22	16.9	35			
			10	30.6	0.76	40.0	69			
200	1.5×10^3	4.225	0	763	62.1	12.3				
			1-1/3	438	10.7	40.9	70.0	0.00092	0.37	0.25
200	1.4×10^3	4.483	0	474	14.8	32.0				
			2-2/3	405	0.085	4.8×10^3	99.4	0.0055	3.62	0.15
200	1.4×10^3	4.117	0	429	28.3	15.2				
			4	411	0.164	2.51×10^3	99.4	0.0044	0.66	0.67
200	1.6×10^3	4.456	0	504	39.5	12.8				
			10	472	0.0243	1.94×10^4	99.9		-	-
300	1.6×10^3	3.810	0	477	48.3	9.90				
			1-1/3	397	0.114	3.48×10^3	99.7	0.00098	1.08	0.091
300	1.6×10^3	4.218	0	456	26.4	17.3				
			2-2/3	474	0.0772	6.17×10^3	99.7	0.00172	0.65	0.26
300	1.6×10^3	4.644	0	445	37.4	11.9				
			4	406	0.147	2.76×10^3	99.5	0.0030	0.84	0.36
300	1.5×10^3	5.370	0	511	38.6	13.2				
			10	472	0.13	3.63×10^3	99.6	0.0081	0.60	1.3

^aOne hour of circulation time is equivalent to 0.66 min of residence time of the entire sample in the decomposition vessel

^bPercentage Pu removed from gas $\frac{(Pu/U)_{initial} - (Pu/U)_{final}}{(Pu/U)_{initial}} \times 100$

^cThis does not include the quantity of plutonium deposited as tetrafluoride in the vessel prior to each experiment

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

The best separation was obtained at 200 C when a gas mixture with an initial ratio of uranium to plutonium of 12.8 was circulated through the decomposition vessel for 10 hours (The circulation time of 10 hours was equivalent to a residence time in the vessel of 6.6 min for the entire mixture) The uranium to plutonium ratio increased to 1.94×10^4 during this period, indicating a removal of 99.9 percent of the initial plutonium from the gas. At 300 C, the maximum ratio of uranium to plutonium in the gas phase was reached much more rapidly. Circulation of the gas phase through the decomposition vessel at 300 C for $1\frac{1}{3}$ hours (residence time, 0.88 min) increased the uranium to plutonium ratio in the gas mixture from 9.90 to 3.48×10^3 , indicating a removal of 99.7 percent of the initial plutonium from the gas phase.

The percentage of uranium in the deposited plutonium tetrafluoride increased with increased total circulation time (or residence time of the total gas mixture in the hot vessel) for the set of experiments at 300 C. The purest plutonium tetrafluoride product was obtained when a gas mixture with an initial concentration of 90.8 percent uranium hexafluoride in total hexafluorides was circulated for $1\frac{1}{3}$ hours (residence time of total mixture, 0.88 min) through a vessel heated to 300 C. The uranium content in the deposited plutonium tetrafluoride was 0.091 percent. The results indicate that thermal decomposition can be used to obtain a separation of plutonium hexafluoride from uranium hexafluoride.

In an effort to explain the presence of the small amount of uranium in the deposited plutonium tetrafluoride, experiments were carried out to determine whether uranium hexafluoride undergoes thermal decomposition at 300 C. The experiments were performed in cylindrical nickel vessels made from seven-inch lengths of two-inch diameter nickel pipe. The equipment included nickel diaphragm valves and thermowells. All of the joints were Heliarc-welded. The vessel, after a prefluorination treatment, was filled with about 100 mm Hg of uranium hexafluoride gas at room temperature. The vessel was then rapidly heated to the reaction temperature of 333 C and held at this temperature for several hours. In the course of one series of experiments, it was noted that a gas, noncondensable at -196 C, was present with the remaining unreacted uranium hexafluoride. This gas was found by mass spectrographic analysis to contain 94.1 percent oxygen, 3.6 percent nitrogen, and 2.3 percent water. A solid product, uranium tetrafluoride, was located only near weld areas, which suggested a corrosion reaction. Since the observations could be accounted for by a reaction between uranium hexafluoride and nickel oxide (which is probably formed on the interior of the vessels during the welding operations), it was concluded that the reaction which uranium hexafluoride underwent was not a thermal decomposition. The absence of evidence of thermal decomposition of uranium hexafluoride in this study indicates that thermal decomposition of uranium hexafluoride is not the source of uranium found in the deposited plutonium tetrafluoride.

4. Separation of Plutonium Hexafluoride from Off-Gases

Investigations were continued to determine the efficiency of removal of accidentally released plutonium hexafluoride from the exhausts of ventilation systems in order to avoid any possible release of plutonium hexafluoride from experimental facilities to the atmosphere. Factors affecting the vapor phase hydrolysis of plutonium hexafluoride and the filtration of plutonium particulate matter obtained from the hydrolysis have been studied. The filters evaluated were AEC type filters used in glove-box installations at Argonne National Laboratory. Particle penetration data were obtained from experiments in which small-scale controlled releases of plutonium hexafluoride, 25 mg or less, were made into air atmospheres of known moisture content. The resulting air mixtures were passed through

AEC filters, a water bubbler, and Millipore filters in series, at a controlled flow rate. Gamma and/or alpha counts of the filters and bubbler were used to determine penetration for individual and combinations of filters.

Figure II-7

FRACTION OF RELEASED PLUTONIUM HEXAFLUORIDE PASSING THROUGH TWO AEC FILTERS

In Figure II-7 the log of the ratio of plutonium passing through two AEC filters to the plutonium released is plotted against the log of the ratio of moles of plutonium hexafluoride to moles of water initially present in the mixing chamber.

The amount of plutonium hexafluoride released varied between 1.5 and 25 mg. The partial pressure of water in the air used varied between 0.77 and 10.64 mm Hg. The air velocity through the filters was 1.0 cm per sec in all experiments. When there was sufficient moisture in the air to hydrolyze completely the plutonium hexafluoride released, the penetration of two AEC filters in series varied

from one part per million to two parts per billion. It has been assumed, extrapolating the information obtained from these experiments, that the Argonne glove-box installations can safely handle up to fifty grams of plutonium hexafluoride when the partial pressure of the water in the air atmosphere of the box is in excess of 6.8 mm Hg.

The sizes of particles produced by the vapor phase hydrolysis of plutonium hexafluoride were determined by examination with an electron microscope. Samples of the material were collected by an electrostatic precipitator and by AEC filter media. Most of the hydrolyzed plutonium hexafluoride was found in the form of agglomerates. The agglomerates observed had a wide size range and were composed of spherical particles from 0.1 to 0.2 micron diameter.

5. Radiation Chemistry of Plutonium Hexafluoride

Plutonium hexafluoride formed in the Direct Fluorination Volatility Process will be subject to gamma radiation from fission products. A study of the radiation chemistry of plutonium hexafluoride has been continued to determine the extent of decomposition of plutonium hexafluoride by gamma radiation. Samples of gaseous plutonium hexafluoride, contained in thin-walled nickel vessels, were irradiated in the Argonne High-Level Gamma-Irradiation Facility, by gamma radiation from spent reactor fuel elements. Plutonium hexafluoride decomposed to elemental fluorine and plutonium tetrafluoride under the influence of gamma radiation. Data obtained showed an increase of the extent of decomposition with increasing amounts of energy absorbed in plutonium hexafluoride as shown in Figure II-8. Plutonium tetrafluoride and fluorine were identified as the products of the decomposition. The G value for the decomposition is 7 molecules of plutonium hexafluoride decomposed per 100 ev absorbed. Decomposition by gamma radiation from fission products at the energy level to be expected in process vessels should not cause any difficulties in the Direct Fluorination Volatility Process.

Figure II-8

DECOMPOSITION OF PLUTONIUM HEXA- FLUORIDE BY GAMMA RADIATION $\bar{E}_\gamma = 0.75 \text{ Mev}$

The rate of decomposition of plutonium hexafluoride by its own alpha radiation has been calculated for spherical vessels of 3.175-cm radius using the G value for the decomposition of plutonium hexafluoride by gamma radiation. In Tables II-3 and II-4, the calculated values (see ANL-6596, pages 132 to 135 for method of calculation) are compared with experimental values obtained at Argonne and with literature values of experimentally determined decomposition rates.

Table II-3

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

Energy of the alpha particles: 5.15 Mev
Radius of spherical container: 3.175 cm
G = 7 PuF₆ molecules decomposed/100 ev

Pressure PuF ₆ (mm Hg)	Range ^a (cm)	Decomposition (Percent per Day)	
		Calculated	Observed
28	24.21	0.23	0.06 - 0.35 ^b
50	12.52	0.43	0.22 ± 0.08 ^c
100	6.76	0.93	0.32 ± 0.08 ^c
1000	0.67	2.92	-
solid	0.002	3.21	1.5 ^b 1.3 ^d 2.0 ^e

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

^bWeinstock, B. and Malm, J. G., J. Inorg. Nucl. Chem. 2, 380 (1956).

^cAverage experimental values from Table II-4.

^dFlorin, A. E., Tannenbaum, I. R., and Lemons, J. F., J. Inorg. Nucl. Chem. 2, 368 (1956).

^eMandleberg, C. J. et al., J. Inorg. Nucl. Chem. 2, 358 (1956).

Table II-4

SUMMARY OF DATA ON DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE BY ITS ALPHA RADIATIONSpherical Vessels: Volumes: 119-137 ml
Radii: 3.04-3.18 cm

Vessel Material	Temp (C)	Pressure (mm Hg)	Initial PuF ₆ (mg) ^a	Decomposition (Percent per Day) (No. of Days)							
				5.6	12.6	21.9	157.7	175.9	229	327	386
Nickel	26	50	116-119	-	0.30 ^b	-	0.13 ^b	-	0.16	-	-
Nickel	26	100	227-236	0.37 ^b	0.36 ^b	-	0.13 ^c	0.23 ^b	0.16	0.080	0.076
Pyrex	26	100	254-261	-	-	-	-	0.34 ^b	-	-	-
Quartz	26	100	216-221	-	-	-	-	0.23 ^b	-	-	-
Aluminum	82	87-88	178-181	-	-	0.78 ^b	-	-	-	-	-
Aluminum	82	787	1616	-	-	0.81	-	-	-	-	-
Nickel	82	797	1636	-	-	1.10	-	-	-	-	-
Nickel	82	94	193	-	-	0.97	-	-	-	-	-

^aCertain values have been given as ranges since the decomposition conditions were not exactly the same for the several experiments reported in each column.^bAverage of two well-agreeing values.^cTime 156.7 days instead of 157.7 days.

Average decomposition rates of plutonium hexafluoride at about 26 C in 125 to 128 cc nickel spheres for 229 and 386 days were 0.16 and 0.076 percent per day, respectively, when the initial plutonium hexafluoride pressure was 100 mm Hg. Several spheres contained 98 mm Hg of plutonium hexafluoride which decomposed at the rate of 0.083 and 0.091 percent per day for 327 days. When 50 mm Hg of plutonium hexafluoride was used, rates of 0.19 and 0.16 percent per day were found for 232- and 229-day runs, respectively. The average rate of plutonium hexafluoride decomposition was found to decrease with increasing storage time.

Plutonium hexafluoride decomposition rates were also studied in the presence of either helium, krypton, fluorine, oxygen or nitrogen in runs of about 230-day duration. The rates for 100 mm Hg of plutonium hexafluoride in the presence of 2.7, 0.8 and 0.8 atmospheres of helium were 0.11, 0.14 and 0.12 percent per day, respectively. Under similar conditions, 4.9, 0.9 and 0.9 atmospheres of krypton decreased the rates to 0.11, 0.073 and 0.081 percent per day, respectively. Fluorine depressed the decomposition rates to 0.026 and 0.029 percent per day for 2.8 and 0.8 atmospheres of fluorine, respectively. In two runs with oxygen at 0.9 atmosphere, rates of 0.060 and 0.077 percent plutonium hexafluoride decomposed per day were obtained. With 3 atmospheres of oxygen, however, 93.7 percent of the plutonium hexafluoride decomposed. When nitrogen was used, nitrogen trifluoride was formed and the plutonium hexafluoride was 78.7, 92.1 and 96.9 percent decomposed in 2.7, 0.8 and 0.8 atmospheres of nitrogen, respectively.

6. Reactions of Fluoride Compounds

Experiments have been carried out to determine whether plutonium compounds react with fission product element compounds during fluorination. Knowledge of such interactions would be useful for the understanding of the mechanism whereby plutonium is retained on inert solids in the presence of fission products. Mixtures of plutonium dioxide and plutonium tetrafluoride with the oxides and fluorides of barium, zirconium, lanthanum, neodymium, praseodymium, cerium, and cesium were reacted with fluorine at 450 C for 10 hours. Analyses of the fluorination products were made by X-ray diffraction and in some cases by conventional chemical means. Possible compound formation has been indicated for the plutonium-barium and the plutonium-cesium systems. Experimental evidence suggests that the double compounds most probably formed are BaPuF_6 and Cs_2PuF_6 . In the plutonium-cerium and plutonium-zirconium systems, in which all the components form tetrafluorides, the formation of solid solutions is possible.

Cathers and Jolley at Oak Ridge National Laboratory (USAEC Report ORNL-3298) indicated that plutonium hexafluoride and calcium fluoride react to form a complex and that this reaction could be used to remove plutonium hexafluoride selectively from a gas stream containing uranium hexafluoride and plutonium hexafluoride. An investigation of the reaction was undertaken to assess its possible utility in a separations process.

An 0.4-gram sample of powdered, prefluorinated calcium fluoride was treated with an equal weight of plutonium hexafluoride so that both solid and gaseous plutonium hexafluoride were in contact with calcium fluoride. After one hour at room temperature, followed by vacuum distillation of plutonium hexafluoride, only 0.7 percent of the initial plutonium hexafluoride remained on the calcium fluoride. It is concluded that calcium fluoride does not form a complex with plutonium hexafluoride that is stable under these conditions. However, it is possible that a compound can be formed whose decomposition pressure is high.

A number of reactions of fluoride compounds have been studied to gain basic information on the chemistry of these compounds or to evaluate the possibility of adapting some of the reactions to analytical chemistry. These reactions are briefly discussed below.

The reaction between uranium hexafluoride vapor and hydrogen sulfide gas was investigated for possible analytical use. The reaction was found to take place readily at 25 C to produce uranium tetrafluoride, sulfur tetrafluoride, and hydrogen fluoride. When the reaction temperature was 100 to 500 C, free sulfur and sulfur hexafluoride formed in addition to the above products.

The reactions of carbon disulfide with uranium hexafluoride and plutonium hexafluoride were investigated. Uranium hexafluoride was found to react readily with carbon disulfide at room temperature. When the reaction was allowed to proceed to completion at room temperature, the main gaseous products were $(\text{CF}_3)_2\text{S}_2$ and $(\text{CF}_3)_2\text{S}_3$, with traces of sulfur tetrafluoride. With excess uranium hexafluoride, the solid reaction product was U_2F_9 . When the temperature of the reaction mixture was 100 to 200 C, the gaseous products were sulfur tetrafluoride, sulfur hexafluoride, tetrafluoromethane, and $(\text{CF}_3)_2\text{S}_2$, and possibly $(\text{CF}_3)_2\text{S}_3$. Plutonium hexafluoride was also found to react readily with carbon disulfide at room temperature. The solid product of the reaction was plutonium tetrafluoride, and the gaseous products were found to be sulfur tetrafluoride, sulfur hexafluoride, and tetrafluoromethane.

It was demonstrated that mercury reacts quantitatively with plutonium hexafluoride in a glass vessel at 25 C. Although the product of the reaction was not identified, it is likely that the product was plutonium tetrafluoride. Plutonium was recovered from the mercury by extraction with a solution containing 4 molar nitric acid and 0.1 molar aluminum nitrate. The plutonium was extracted from the aqueous solution with hexone and analyzed by alpha counting. The original sample contained 47 mg of plutonium, weighed as plutonium hexafluoride. Assay by alpha counting indicated the presence of 48 mg of plutonium.

As a basic study, attempts have been made to prepare mixed chlorofluorides of hexavalent uranium by the reaction of sulfur tetrafluoride with uranyl chloride. This would be analogous to the preparation of uranium hexafluoride from uranyl fluoride and sulfur tetrafluoride. Attempts to prepare the mixed chlorofluorides of uranium resulted in the formation of uranium tetrafluoride.

7 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 hexafluoride, the absorption spectrum of gaseous plutonium hexafluoride was determined in the ultraviolet, visible, and near infrared region and extinction coefficients were calculated. Major peaks in the spectrum were observed in the ultraviolet, visible, and the near infrared regions. Absorption in the ultraviolet shows several strong bands, one close to the limits of the instrument at 2000 Å and others at 2250 Å, 2500 Å and 3155 Å. Several peaks are evident in the visible region between 4100 Å and 5800 Å. The major peaks in the near infrared region are grouped into two bands, one at approximately 8000 Å and the second at approximately 10,000 Å. Peak spacings in the near infrared region were correlated with the known vibrational frequencies, and positions of the bands were correlated with the absorption spectra of the isoelectronic series U(IV), Np(V) and Pu(VI).

III. CALORIMETRY

Thermodynamic data are lacking for many compounds of interest in high-temperature chemistry because of the experimental difficulties involved in making the necessary measurements. For example, heats of formation of the tetrafluorides of hafnium and zirconium were not available in the literature, but were determined after the Calorimetry Group developed the appropriate techniques. Part of the program of the group consists of determinations of heats of formation by oxygen bomb calorimetry. However, many of the compounds of interest are difficult to burn in oxygen and, consequently, cannot be studied by oxygen bomb calorimetry. To study compounds of interest that are difficult to burn in oxygen, the techniques have been modified so that fluorine can be used as the oxidant.

Heats of formation at 25 C from oxygen or fluorine bomb calorimetry will be combined with heat content data measured with a high-temperature enthalpy calorimeter to determine thermodynamic properties at high temperatures. A high-temperature enthalpy calorimeter is under construction and is expected to be ready for final testing at the end of 1963.

A. Oxygen Bomb Calorimetry

The heat of formation values for zirconium dihydride and zirconium dideuteride reported previously (-37.72 ± 0.72 kcal/mole and -39.00 ± 0.64 kcal/mole, respectively) have been redetermined with new preparations of lower oxygen impurity content used as samples. Analysis of the previous data had indicated that there was considerable uncertainty in the results due to oxygen impurity in the samples. With the new preparations, the thermal correction resulting from the oxygen impurity was less than 0.2 percent of the total measured heat. The new values obtained for the heats of formation follow.

$$\Delta H_{298}^0 (\text{ZrH}_2) = -38.90 \pm 0.31 \text{ kcal/mole}$$

$$\Delta H_{298}^0 (\text{ZrD}_2) = -40.22 \pm 0.27 \text{ kcal/mole}$$

The sample support arrangement for combustion of each of these materials is shown in Figure III-1. The sample was contained in a sealed Mylar bag, which rested on a pressed zirconia disc in a platinum dish. The dish or crucible rested on a heavy platinum plate and was surrounded by a platinum shield. At the start of the experiment, the bomb also contained one ml of water in a platinum thimble and 15 atm of pure oxygen. Ignition of the cotton thread fuse was accomplished by heating

the platinum ignition wire to red heat with a known amount of electrical energy. Under these conditions, the sample burned completely to zirconium dioxide and water or to zirconium dioxide and deuterium oxide.

Figure III-1

COMBUSTION BOMB WITH SAMPLE-SUPPORT
ARRANGEMENT FOR OXYGEN COMBUSTION
OF ZIRCONIUM DIHYDRIDE OR ZIRCONIUM
DIDEUTERIDE

B. Fluorine Bomb Calorimetry

The heat of formation of uranium hexafluoride has been of interest to the Atomic Energy Commission since the early days of the Manhattan Project, when Long and Davidson¹ determined the heat of solution of UF_6 and from this calculated a heat of formation value. Since then, Russian workers² have made confirmatory measurements. The latest critical review³ of the thermodynamics of uranium compounds, put out under

¹Long, F. A. and Davidson, N. R., reported in J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 412.

²Popov, M. M., Kostylev, F. A. and Karpova, T. F., Zhur. neorg. Khim. 2, 9 (1957).

³Rand, M. H. and Kubaschewski, O., British Atomic Energy Report AERE-R-3487 (1960).

contract with the United Kingdom Atomic Energy Authority, gives a "selected" value of -523 ± 6 kcal/mole for the heat of formation of crystalline uranium hexafluoride based on the earlier work. Because of the large uncertainty associated with the "selected" value, this laboratory undertook a redetermination by the direct means of fluorine bomb calorimetric combustions of uranium. A value that was more reliable was particularly needed as an important auxiliary datum for anticipated determinations of the heats of formation of other uranium compounds by fluorine bomb calorimetry. Tentative results of the direct determination, presented below, do not significantly change the "selected" value, but the uncertainty in the value is now one whole order of magnitude less.

$$\Delta\text{Hf}_{298}^0 (\text{UF}_6) = -522.5_7 \pm 0.4_4 \text{ kcal/mole}$$

$$\Delta\text{Hf}_{298}^0 (\text{UF}_6) = -510.7_0 \pm 0.4_6 \text{ kcal/mole}$$

Within the past year, determinations also have been made of the heats of formation of MgF_2 , CdF_2 , AlF_3 , and ZnF_2 .

$$\Delta\text{Hf}_{298}^0 (\text{MgF}_2) = -265.0 \pm 0.7 \text{ kcal/mole}$$

$$\Delta\text{Hf}_{298}^0 (\text{CdF}_2) = -167.5 \pm 0.2 \text{ kcal/mole}$$

$$\Delta\text{Hf}_{298}^0 (\text{AlF}_3) = -356.5 \pm 0.7 \text{ kcal/mole}$$

$$\Delta\text{Hf}_{298}^0 (\text{ZnF}_2) = -183.0 \pm 0.3 \text{ kcal/mole}$$

Calorimetric combustions of RuF_5 , TaF_5 , NbF_5 , and ZrB_2 have been performed, but calculations of their heats of formation are not yet complete. Techniques for the combustion of uranium monosulfide in fluorine, carbon in fluorine, and silicon carbide in fluorine are being developed.

Sample Supports for Fluorine Bomb Calorimetry

An important problem in fluorine bomb calorimetry has been the development of satisfactory support arrangements for the combustion

samples. For combustions of molybdenum in fluorine,⁴ the sample was suspended by molybdenum wire from relatively heavy nickel supports. The only contact of the burning sample with the nickel support was at the wire, and negligible reaction with the support occurred.

For the combustions of many of the metals studied, the sample was in the form of a vertical rod, of which only the top portion was consumed by the reaction. In these combustions, the burning sample was in effect supported by unburned sample, and contact between the sample and the support was in a relatively cool zone. Negligible reaction with the sample support occurred. The studies of RuF_5 , TaF_5 , NbF_5 , and UF_6 were carried out by the vertical rod support technique.

For combustions of several materials, support plates were used. For zirconium diboride, a heavy zirconium plate was used. Some reaction of the zirconium plate with fluorine occurred. However, a thermal correction for this reaction could be made accurately. For alpha-quartz, a nickel support plate was used. The alpha-quartz burned at a low enough temperature so that negligible reaction with the support plate occurred.

For the combustions of the softer metals (cadmium, magnesium, aluminum and zinc), none of the above techniques were satisfactory - principally because the samples melted during combustion so that containment of the sample and reaction of the molten metal with the support became serious problems. For these metals, support discs were made of the metal fluorides - preferably the fluoride of the metal studied. The development of techniques for the fabrication and use of these discs proved to be difficult and time-consuming. Nevertheless, this year's accomplishments include the development of techniques and the calorimetric combustion of cadmium, magnesium, aluminum, and zinc.

Experience gained thus far provides a basis for choosing sample support techniques. At the start of an investigation, trial combustions are made in a transparent-wall reaction vessel, the burning characteristics of the sample material are observed, and a sample-support arrangement is chosen.

C. High-Temperature Enthalpy Calorimetry

A calorimetric system for measuring changes in enthalpy up to 1500 C is under construction. 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 passes when dropped, and a calorimeter. The calorimeter equipment has been moved into a new laboratory, and assembly and testing have been accelerated.

⁴Settle, J. L., Feder, H. M., Hubbard, W. N., J. Phys. Chem. **65**, 1337 (1961).

The furnace has been tested up to over 1000 C. Most of the work has been concerned with the development of automatic controls for heating the furnace with the objective of maintaining the capsule containing the sample at a constant known temperature. The capsule is surrounded by an inner shield and two shields equipped with heaters. In tests at several temperatures up to 1000 C, the inner shield temperature was maintained constant to ± 0.1 C over a 24-hr period.

In an enthalpy determination, the capsule is brought to temperature equilibrium and then dropped through a cold zone into the calorimeter. It is desirable to minimize the heat loss occurring during the sample drop. This is done by (1) providing a shield that maintains an isothermal zone at the top of the fall path where the capsule falls most slowly and (2) allowing the capsule to fall at an accelerating rate. The capsule is attached by means of a wire to a drop weight (located in the drop tube which extends vertically above the furnace). The drop weight, held at the top of the drop tube during heatup, falls the length of the drop tube when released. This allows the sample to drop into the calorimeter chamber. It is necessary to decelerate the capsule without subjecting the drop wire to too great a stress. In this apparatus, the drop weight falls through a vacuum and therefore is not decelerated by the usual technique of air damping in the drop tube. Rather, the drop weight is a permanent magnet which in falling induces a current in a coil wrapped around the drop tube and thereby triggers an electronic circuit which activates an eddy current brake magnet in the drop mechanism. This mechanism has worked successfully in tests utilizing an assembly consisting of the drop mechanism and gate only.

It is planned to obtain values for heat loss during a drop by two methods, allowing comparison. One method involves the use of a trickle current in the eddy current brake magnet during drops, making it possible to vary the drop speed. It will be possible to make enthalpy measurements at various drop speeds and to extrapolate the values for heat loss so that the enthalpy value in the absence of heat loss may be calculated. The other method of determination is the calculation of the heat transfer by radiation during a drop using known transfer coefficients.

An electron beam furnace is being designed for a similar high temperature calorimeter to measure changes in enthalpy up to 2500 C. The power supply and electron beam guns for the furnace have been delivered and will be set up.

IV. REACTOR SAFETY

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 long-range objective of the metal-water reactions program is to provide a practical means for estimating the rate and extent of reaction that will occur during postulated reactor accidents. The program has been divided into three separate phases as indicated in Table IV-1. The first phase involves the experimental determination of the isothermal rate laws and rate constants. The second phase involves experimental observation of the nonisothermal reaction with small particles in order to simulate accidental situations under idealized conditions. The third and final phase of the program is the development of a mathematical model of metal-water reactions that will combine isothermal rate laws with equations of heat and mass transfer so that the course of the reaction can be computed under any set of initial conditions. An important function of the nonisothermal experiments is to provide a check on computed results and also to detect physical limitations to the reaction rate that would not be apparent in isothermal experiments. In the TREAT experiments, there is a more direct simulation of reactor excursion accidents in which the nature and degree of fragmentation of representative fuel element specimens is determined.

Table IV-1

STATUS OF METAL-WATER REACTIONS RESEARCH PROGRAM

Metal	Phase I Determination of Isothermal Reaction Rate Law				Phase II Study of Nonisothermal Reactions			Phase III Theoretical Calculation of Rate and Extent of Reaction ^a
	Pressure Pulse Method	Volumetric Method	Levitation Melting Method	Other Institution	Condenser Discharge Method	Laser Heating Method	TREAT Studies	
Zirconium	-	-	-	Available 1000-1850 C	Completed	Will be attempted	Work in progress	Some work successfully done
Aluminum	Completed 800-1200 C	-	Completed 1200-1800 C	-	Not applicable	Will be attempted	Work in progress	Will be attempted
Stainless Steel	-	Work in progress ^b	-	-	Completed	Will be attempted	Work in progress	Will be attempted
Uranium	-	Completed ^c 400-1200 C	-	-	Completed	Will be attempted	Work in progress	Work in progress

^aIt is planned to extend these calculations to cases of full-scale reactor accidents.

^bVolumetric method not completely satisfactory and further method development work may be necessary.

^cVery recently completed to 1600 C.

1. Condenser-discharge Experiments

In the condenser-discharge experiment, metal wires are heated in a water environment by a surge current from a bank of condensers. The energy input to the wires is measured electrically and used to calculate the initial reaction temperature. Transient pressures are measured and used to indicate reaction rate. The amount of hydrogen generated gives the extent of reaction, and the particle size of residue indicates the surface area exposed to reaction.

Previous experiments with zirconium wires and with uranium wires showed that reaction in heated water (90 to 315 C) was much more extensive than reaction in room-temperature water. Results with stainless steel wires, plotted in Figure IV-1, have shown that reaction in heated water was only slightly greater than reaction in room temperature water. This finding indicated that the reaction rate is controlled predominantly by a chemical rate law even at very high temperatures and that gaseous diffusion of water vapor through the evolving hydrogen appears to be less important. The total extent of reaction at high initial temperatures of the stainless steel (e.g., 36 percent reaction at an initial metal temperature of 3700 C) also was smaller than that of zirconium (100% at 3700 C) or uranium (100% at 3700 C) under similar conditions. This finding also indicated that the reaction rate is controlled predominantly by a chemical rate law and that gaseous diffusion of water vapor through the evolving hydrogen, shown to be of major importance in the zirconium-water reaction, was less important in controlling the rate of the stainless steel-water reaction.

Figure IV-1

STAINLESS STEEL 316-WATER REACTION BY THE CONDENSER DISCHARGE METHOD

2. Volumetric Experiments

A second laboratory-scale method uses induction heating of metal samples in flowing steam. The quantity of reaction is determined continuously by condensing the effluent steam and measuring the volume of hydrogen generated in the reaction. The samples are supported on stainless steel-clad thermocouples which provide the means of temperature control and measurement. Reactions of one-cm cubes of uranium with steam at about one atmosphere were studied at sample temperatures of 400 to 1200 C. A schematic diagram of the volumetric apparatus is shown in Figure IV-2. Typical results of an experiment at each of the temperatures studied are shown in Figure IV-3. At 400 C, the reaction occurs in two stages, the rates of which are both linear, whereas at 500 C and above the rate law is nearly parabolic.

Figure IV-2
VOLUMETRIC APPARATUS FOR
STUDY OF THE URANIUM-
STEAM REACTION

Figure IV-3
HYDROGEN EVOLUTION IN THE REACTION OF
URANIUM WITH STEAM AT 1 ATMOSPHERE

A plot of the parabolic rate constants as a function of reciprocal temperature, shown in Figure IV-4, indicated that a consistent rate law applies over the temperature range of 600 to 1200 C, despite the fact that uranium undergoes three phase changes in this range.

Figure IV-4

EFFECT OF TEMPERATURE ON THE RATE OF HYDROGEN EVOLUTION FOR THE REACTION OF STEAM WITH URANIUM

The oxide formed on the surface of the uranium cubes was adherent in the 600 to 1200 C range and retained the original polish of the metal surface. The rapid linear reaction at 400 C produced an oxide which was nearly colloidal and powdered off the sample continuously. It was evident that the oxide produced at 400 C afforded no protection to the underlying metal.

3. Levitation Experiments

The levitation method involves the simultaneous heating and levitation of metal pellets in a radiofrequency field. In this method, steam at one atmosphere flows over a nominal $\frac{1}{4}$ -inch metal sphere, which is rapidly heated to the test temperature. Temperature is measured and controlled by a

two-color optical pyrometer. The technique has been applied to the study of the reaction of steam with molten aluminum above 1200 C. Aluminum pellets were exposed to the steam for a fixed period of time. The quantity of reaction was determined gravimetrically by selective dissolution of the unreacted aluminum, leaving the oxide intact.

The results of experiments in which samples did not ignite are plotted in Figure IV-5. Results at 1400, 1500, and 1600 C tended to follow a linear rate law, while the results at 1200 and 1300 C followed a cubic rate law. Also shown in the figure, in dashed lines, are previous results for the aluminum-steam reaction obtained by the pressure-pulse method. Results obtained with both experimental methods indicated that a cubic rate law applies at 1200 C; however, the values of rate constants differed by a factor of two.

Figure IV-5

REACTION OF ALUMINUM WITH STEAM

Data points and solid lines obtained by the levitation melting method. Dashed lines obtained by the pressure pulse method.

At 1600 C ignition occurred after about 18 minutes and at 1700 C after five minutes. Immediate ignition occurred at 1750 C. Ignitions began with the formation of a small hot spot which rapidly spread across the surface of the pellet. Burning appeared to occur by a vapor phase mechanism.

4. Reactor Transient Experiments

The reactions of metal fuel pins in a water environment are studied by subjecting fuel pins containing enriched uranium to a burst of neutrons in TREAT. A stainless steel autoclave contains the fuel pin and water. Both the temperature of the metal and the pressure in the autoclave are recorded by an oscillograph. The metal is melted by the fission heat which the neutron pulse generates. The metal, in turn, reacts with the water. The evolved hydrogen is measured to determine the extent of reaction. Subsequently, particle sizes are determined and metallographic studies are made. These experiments have been conducted on the four metals of principal interest in water reactor technology: aluminum, zirconium, uranium, and stainless steel. Tests have been conducted with fuel pins with a metal core, in both pin and wire form, and with oxide core and cermet cores.

Transients conducted with aluminum-clad, aluminum-23 weight percent uranium core fuel plates (SPERT fuel) and with unclad aluminum-10 weight percent U_3O_8 cermet fuel pins showed a stepwise dependence on

the energy of the reactor burst (Figure IV-6). The extent of aluminum-water reaction shown in Figure IV-6 may correlate with results of isothermal oxidation studies of aluminum shown in Figure IV-5. The very slow cubic oxidation occurring below 1400 C accounts for the very small reaction obtained in reactor transients with less than 430 cal/g energy input. The vigorous linear oxidation occurring between 1400 and 1750 C might be identified with the in-pile specimens that received energy inputs between 430 and 794 cal/g. The vapor phase ignitions occurring at temperatures above 1750 C would then account for the large amount of reaction occurring during the most vigorous transients of the series. It is expected that a more rigorous correlation between the results of in-pile studies and isothermal oxidation studies by the levitation method can be achieved by a mathematical study similar to the one previously applied to the zirconium-water reaction.

Figure IV-6

PERCENT OF METAL REACTED VERSUS NUCLEAR ENERGY INPUT, cal/g FOR 2S ALUMINUM-CLAD, 77 w/o ALUMINUM-23 w/o URANIUM (FULLY ENRICHED) PLATES AND UNCLAD 90 w/o ALUMINUM, 10 w/o U_3O_8 CERMET PINS

Evidence of the increasing damage suffered by fuel plates subjected to increasingly energetic reactor transients is presented in Figure IV-7. The least energetic transient imparted 174 cal/g to the fuel plate and caused only a slight indication of melting. A transient which imparted 652 cal/g resulted in fragmentation and caused individual particles to be welded to various parts of the autoclave. Still more energetic transients caused more extensive fragmentation.

Figure IV-7

FIVE ALUMINUM CLAD, 77 w/o ALUMINUM-23 w/o URANIUM
(FULLY ENRICHED) CORE PLATES AFTER TRANSIENT
BURSTS IN TREAT

(Original size, 0.06 x 0.5 x 1.4 inches)

B. Metal-Oxidation and Ignition

The increased handling of reactor metals concomitant with 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, plutonium, and other metals and compounds are being studied in order to clarify the factors governing the pyrophoric characteristics of these materials. This knowledge should reduce the hazards associated with shipping, fabricating, and processing these nuclear reactor materials.

Subjects studied to date are indicated in Table IV-2. Future research will be concentrated on plutonium and pre-irradiated uranium.

Table IV-2

STATUS OF METAL OXIDATION AND IGNITION KINETICS PROGRAM

	Phase I	Phase II				Phase III			
	Isothermal Oxidation Rates ^a	Ignition				Air Burning			
		Single Pieces ^a		Powder		Temperature Measurement		Propagation Rates	
		Exp	Theo	Exp	Theo	Exp	Theo	Exp	Theo
Zirconium	400-900 C in O ₂ completed	Completed	Completed ^b	Partially done	-	Completed	Completed ^c	Completed	Completed ^c
Uranium	125-625 C in O ₂ completed 600-1000 C in Air in progress	Unirradiated completed, irradiated in progress	Completed ^b	Completed	Completed ^b	Completed	Completed ^c	Completed	Completed ^c
Plutonium	140-450 C in O ₂ completed Above 450 C in O ₂ in progress	In progress	-	-	-	-	-	In progress	-

^aIncludes studies with a large number of binary alloys.^bIgnition temperatures calculated from isothermal rate data.^cBurning temperatures and propagation rates calculated from heat transfer theory.1. Uranium Ignitions

Preliminary studies of the isothermal oxidation of uranium in the range of 300 to 600 C were reported previously. More recent studies have shown that an accelerating oxidation occurs below 450 C while a decelerating reaction (due to the formation of protective oxide) occurs above 450 C. The oxidation of pure uranium could be described by the following empirical equations:

Temp Range (C)	Rate Equation
300 < T < 450	$w^{4/5} = 2.6 \times 10^7 t (\exp -16,800/RT)$
T > 450	$w^{6/5} = 7.3 \times 10^7 t (\exp -14,300/RT)$

where: w is quantity of oxygen reacted ($\mu\text{g}/\text{sq cm}$) and t is time in minutes.

The equations were used in conjunction with a simple heat balance to compute the course of ignitions. Temperature-time curves corresponding to the rising temperature ignition experiment (burning curves) were computed for specimens of various specific surface areas. Ignition temperatures obtained graphically from computed temperature-time curves are compared with ignition temperatures of uranium pieces of a variety of shapes in Figure IV-8. Both experimental and theoretical ignition temperatures undergo a sharp break in the specific area range between 2 and 10 sq cm/g. It is now clear that this unusual behavior results from the change from an accelerating to a decelerating reaction at 450 C.

Figure IV-8
DEPENDENCE OF URANIUM IGNITION ON
SPECIFIC AREA

A series of isothermal oxidation experiments were carried out with pure uranium from two sources and with two alloys of uranium, one containing 1 atom percent aluminum and one containing 1 atom percent copper. Ignition studies had shown that the addition of aluminum decreased the ignition temperature of uranium cubes by 200 C, while the addition of copper increased the ignition temperature by 200 C (see ANL-5974, p. 24). Oxidation rates after 10 mg oxygen/sq cm reaction are plotted as a function of temperature for the four metals in Figure IV-9. The pure metals each showed the transition to a protective oxide and a slower reaction rate at about 450 C; however, the BMI metal (prepared at Battelle Memorial Institute) showed a more gradual transition than the ANL metal. The presence of aluminum inhibited the transition entirely, while the presence of copper enhanced the protectiveness of the post-transition oxide coat.

Inhibition of the transition to a protective oxide at 450 C caused by aluminum additions explained the lower ignition temperature obtained with aluminum-uranium alloys. The higher ignition temperatures obtained with copper alloys were explained by the increased protectiveness of the oxide formed above 500 C. It was possible, on the basis of these two effects, to account for the effects on ignition behavior of alloying with 24 different elements. Low-level binary alloys with aluminum, beryllium, bismuth, carbon, lead, molybdenum, niobium, palladium, platinum, ruthenium, silicon, tantalum, titanium, and vanadium showed complete or partial inhibition of the transition to a protective oxide at 450 C. Some of the nobler metals studied, bismuth, copper, molybdenum, lead, palladium,

platinum, ruthenium, and vanadium, caused increased protectiveness of the post-transition oxide, while additions of cerium, chromium, hydrogen, iron, nickel, rhodium, silver, tantalum, thorium, and zirconium had no effect on the ignition behavior of uranium.

Figure IV-9

RATES OF OXIDATION OF VARIOUS URANIUM SPECIMENS AS A FUNCTION OF TEMPERATURE AFTER 10,000 μg OXYGEN/SQ CM TOTAL OXIDATION

2. Plutonium Studies

Studies of the isothermal oxidation and ignition of plutonium and plutonium alloys are being carried out using a recording thermobalance located in special glove box facilities (see Figure IV-10). Isothermal oxidation experiments were carried out with the alpha, beta, and

gamma phases of plutonium over the temperature range from 100 to 393 C. Oxidation of the alpha phase by oxygen at 100 C indicated that a protective oxide coat was formed; virtually no reaction occurred after 120 minutes. Oxidation of the beta phase at 185 C by oxygen occurred in two stages, both of which showed linear reaction rates, in agreement with British results.¹ First-stage rates were temperature-dependent, as indicated in Figure IV-11, whereas second-stage rates were not. Reaction rates in the gamma phase at 220 to 240 C were linear and appeared to be consistent with the rate observed in the first stage of the beta phase oxidation.

Figure IV-10

THERMOGRAVIMETRIC APPARATUS FOR ISOTHERMAL
OXIDATION STUDIES OF PLUTONIUM

Ignition temperatures of 0.5-cm cubes of plutonium and 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 oxidant. As the rate of reaction

¹Dempsey, E. and Kay, A. E., J. Inst. Metals 86, 379 (1958).

increases, the sample self-heats and finally ignites. The temperature at which the sample ignites is determined by a graphical method. Plutonium samples with a specific area of approximately 0.7 sq cm/g were found to ignite at about 500 C in oxygen and 510 C in air. The addition of a nominal two percent of an additive to the plutonium was found to increase these ignition temperatures only slightly in the case of aluminum, copper, and silicon; the greatest increase (about 80 C in both oxygen and air) in ignition temperatures was caused by the addition of aluminum. Additions of magnesium, chromium, iron, zinc, cerium, and uranium had a negligible effect on the ignition temperatures of plutonium. Plutonium alloys with manganese, cobalt, or nickel ignited at temperatures 30 to 40 C below the ignition temperatures of plutonium.

Figure IV-11

PLUTONIUM LINEAR OXIDATION DATA

3. Burning Studies

Burning temperatures and rates were computed for uranium and zirconium in air on the assumption that burning is controlled by gas-phase diffusion. In this model of burning, the metal rapidly consumes the

oxygen in a thin boundary layer surrounding the sample. Further reaction is then limited by the rate at which oxygen can diffuse through the nitrogen boundary layer. The method of calculation uses correlations of natural-convection and forced-convection heat transfer rates and diffusion rates. The diffusion rate, which is also the reaction rate, is used in an overall heat balance which involves the burning temperature. Calculated burning temperatures were found to depend on the size and shape of the specimen, on the air flow velocity in the forced-convection case, and on the heat of formation and total emissivity of the oxide formed. Calculated burning temperatures in air compared favorably with measured values for zirconium, uranium, and 15 atom percent titanium-zirconium foils, as shown in Figure IV-12.

Figure IV-12

THEORETICAL AND EXPERIMENTAL FOIL BURNING TEMPERATURES IN AIR

Theoretical burning calculations were extended to the computation of the velocity of burning propagation along foils and wires of zirconium and uranium. The theory is similar to one used to describe gaseous flame propagation. Propagation occurs by heat conduction ahead of the burning zone. Reaction rates and burning temperatures were computed on the basis of the gas phase diffusion model of burning. Computed propagation rates for uranium foils and wires showed reasonable agreement with experimentally determined values (Figure IV-13). The calculations also provide an explanation of the failure of propagation to occur in specimens having too great a cross section.

Figure IV-13

EFFECT OF WIRE DIAMETER OR FOIL THICKNESS
ON PROPAGATION VELOCITY FOR URANIUM
WIRES AND 0.3-cm WIDE URANIUM FOILS

4. Group Participation in Project SIFTOR

L. Baker, Jr. and R. C. Liimatainen of the Metal-Water Reactions Group have been engaged in the preparation of a chapter entitled "Chemical Reactions" for inclusion in the book Safety Information for the Technology of Reactors. This book is an attempt to gather in one place all information that is pertinent to the safety of nuclear reactors. The book is being compiled for the AEC by members of the Nuclear Engineering Department of MIT. It is intended that the chapter "Chemical Reactions" summarize the knowledge concerning slow or corrosive reactions as well as rapid or violent reactions that might occur in nuclear reactor systems of all kinds.

V. ENERGY CONVERSION

Work on the direct conversion of heat from nuclear reactors or from other sources into electricity is being continued. Two main avenues of research are being explored: the first is the study of thermally regenerative emf cells; the second is the study of the thermocouple effect.

A. Thermally Regenerative Emf Cells

The objective of the studies on the regenerative emf cells is to produce a device which would operate continuously in a closed Carnot

Figure V-1

TEMPERATURE-ENTROPY DIAGRAM
IN THE REGENERATIVE EMF-CELL
CYCLE

cycle. In this cycle, heat would be consumed in one isothermal leg and useful electrical energy would be produced in the second isothermal leg. Such a thermodynamic cycle is illustrated by a temperature-entropy diagram in Figure V-1. In the diagram, a galvanic cell is arbitrarily placed in the isothermal path 3-4, where the cell reaction $A + B \rightarrow AB$ occurs at temperature T_1 . The temperature of the cell product AB is raised to T_2 along the path 4-2. The product AB is dissociated along the isothermal path 2-1 at temperature T_2 to produce the cell reactants A and B. Since spontaneous recombination of A and B would occur in a

homogeneous system at T_1 , it is necessary to separate the reactants at or near T_2 . The reactants A and B are returned to their respective anode and cathode compartments in the cell and the temperature of the reactants is returned to T_1 along the path 1-3. The maximum overall efficiency of this cycle is the Carnot efficiency which is given by the following equation:

$$\text{Carnot efficiency} = \frac{T_2 - T_1}{T_2}$$

where T is in the Kelvin scale. Although the regenerative cell is not expected to be more efficient than a conventional steam plant (overall conversion efficiencies of about 40 percent have been achieved with conventional generating systems), some of the anticipated advantages of the cell are compactness, versatility with respect to size, low mass to power output, and elimination of most of the mechanical parts which should result in a cell that is long-lived and trouble-free.

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

1. Regenerative Hydride Cell Studies

The first cell selected for study was the lithium hydride cell (see Figure V-2). In operation, the chemical reaction at the molten metal lithium anode is the oxidation of the metal to lithium ions and the reaction at the cathode is the reduction of hydrogen gas to hydride ions. The over-all cell reaction is

Figure V-2

LITHIUM HYDRIDE CELL

The selection of this cell for initial investigation was made after a careful study of the available, though scant, literature.¹ From this study, it appeared that the lithium hydride cell held considerable promise if the difficulties associated with the use of porous metal frits for the hydrogen gas electrode could be eliminated. The difficulties attending the use of porous metal frits were the occurrence of variable catalytic activity at the surface of the frits and alternate flooding of the frits by hydrogen gas and fused salt electrolyte. Despite these difficulties, a current density of 200 amp/sq ft of electrode area at 0.3 volt at a cell operating temperature of 570 C was achieved by a cell developed by the Mine Safety Appliance Corporation.² The cell consisted of a liquid lithium anode, a lithium fluoride-lithium chloride eutectic as an electrolyte, and a stainless steel cathode. The cathode was in the form of a screen or a porous micrometallic gas electrode. The duration of this current and the conditions under which it was achieved are not known.

Studies on hydride cells have also been carried out by Thompson Ramo Wooldridge, Inc.³ (TRW) in Cleveland, Ohio, under a short contract with the U. S. Air Force. The results of the work at TRW led to the conclusion that iron and niobium are the only materials which possess the requisite characteristics for use as hydrogen diffusion diaphragms, i.e., the rates of diffusion of hydrogen through both materials at 400 to 500 C were appreciable and both materials were compatible with the salt-alkali metal environment of the hydride cell. Most of the work at TRW was carried out with iron diaphragms. However, the results of a single, 45-minute run in which a niobium diaphragm was utilized has also been reported by TRW. This run indicated that current densities of over 1000 amp/sq ft of electrode could be achieved by a lithium hydride cell utilizing a niobium diaphragm. Considerable effort, however, was required to provide a niobium diaphragm free of oxide coating at the operating temperature of the cell.

¹(a)Reports of the Mine Safety Appliance Corporation to the U. S. Army Signal Research and Development Laboratory, Fort Monmouth, N. J. Shearer, R. E., Study of Energy Conversion Devices, Report 1, Progress Report to U. S. Army Signal Research and Development Laboratory, Fort Monmouth, N. J., MSAR-59-119, Oct. 31, 1959; Ibid., MSAR-60-12, Report 2, January, 1960; MSAR-60-56, Report 3, April, 1960; MSAR-60-110, Report 4, August, 1960; MSAR-61-99, Report 7, September, 1961.

(b)U. S. Patent 3,031,518, R. C. Werner and Robert E. Shearer, April 24, 1962.

(c)Ciarlariello, T. A. and R. C. Werner, Fuel Cells Based on Nuclear Reactors, Chemical Engineering Progress, 57, 42 (1961).

²Shearer, R. E., Study of Energy Conversion Devices, Report 7, Progress Report to U. S. Army Signal Research and Development Laboratory, Fort Monmouth, N. J., MSAR-61-99, September 1961.

³(a)ASD-TDR-62-241, Electrode Development Program, Prepared by TAPCO, a Division of Thompson Ramo Wooldridge, Inc., January 23, 1962.

(b)ASD-TDR-62-240, Zero Gravity Separator Development for Regenerative Fuel Cell, Ibid., June (1962).

(c)Snock, D. R., J. M. Fuscoe, S. S. Carlton, Extended Life Fuel Cells for Space, Thompson Ramo Wooldridge, Inc., TAPCO Group, Presentation at the National Aerospace Electronics Conference of the Institute of Radio Engineers, Dayton, Ohio, May (1961).

(d)ASD-TDR-62-18, Regenerative Fuel Cell System, H. J. Schwartz, S. S. Carlton and J. M. Fuscoe, Thompson Ramo Wooldridge, Inc., Cleveland, Ohio, April (1962).

In this respect iron diaphragms offer an advantage inasmuch as the iron oxides formed are reduced to the metal by hydrogen at the cell temperature.

In experiments at Argonne, current densities of about 10 amp/sq ft were achieved using a lithium hydride cell with a 5-mil thick Armco iron diaphragm at a cell operating temperature of 500 C. This value is a factor of ten lower than the current density of 100 amp/sq ft which is usually regarded as being the minimum standard of acceptability. The low current density obtained in these experiments is attributed to the low rate of hydrogen diffusion through the pure iron diaphragm (see Figures V-3 and V-4). To achieve a satisfactory current density, a tenfold increase in the rate of diffusion of hydrogen through the diaphragm is necessary.

Figure V-3

EFFECT OF TEMPERATURE ON
HYDROGEN DIFFUSION THROUGH
A 10 MIL ARMCO IRON DIAPHRAGM

(Unannealed)

Figure V-4

EFFECT OF TEMPERATURE ON
HYDROGEN DIFFUSION THROUGH
A 10 MIL ARMCO IRON DIAPHRAGM

(Annealed in H₂ at 900 C for 2 hr)

Consideration has been given to three methods whereby this increase might be achieved. The first of these depends upon the ionization of the hydrogen gas stream behind the diaphragm; the second depends upon finding a more suitable diaphragm material; and the third depends upon the fabrication of a gas electrode with a sufficiently large area to bring about the tenfold increase in diffusion rate.

The effect of ionization of hydrogen on its rate of diffusion through an Armco iron diaphragm was tested in two experiments. In each experiment, an alpha source (plutonium in the first run and curium in the second run) was placed in the hydrogen gas stream behind the iron diaphragm at a distance of about 2 inches from the diaphragm. The intensities of the alpha sources used in the two runs differed by a factor of about ten. The results of the tests indicated that an increase (about twofold at 400 C) in diffusion rate was obtained by the use of the alpha sources. No appreciable dependency of the diffusion rate on the intensity of the alpha sources was observed. From these results, it was concluded that the ionization of the hydrogen stream could not in itself bring about the required tenfold increase in the rate of diffusion of hydrogen through the iron diaphragm.

The second possibility, namely, the utilization of other materials for the construction of gas electrode diaphragms, is now being investigated. Some of the more promising materials, such as molybdenum-iron alloys, niobium, and vanadium, have presented fabrication problems. The solution of these problems has been undertaken by Battelle Memorial Institute (BMI) under a service contract with Argonne National Laboratory. BMI has thus far supplied diaphragms of 5 and 10 weight percent molybdenum-iron alloys and of pure nickel, tantalum, and niobium. A high-purity vanadium foil has been supplied by Ames Laboratory of USAEC. In evaluation tests conducted at Argonne, it was found that the rate of diffusion of hydrogen through the 10 weight percent molybdenum-iron alloy was slightly lower than the rate through pure iron. The rate of diffusion of hydrogen through the pure vanadium foil supplied by Ames was determined to be 1.16×10^{-1} cc/(sq cm)(sec) at 550 C. This value would allow the achievement of a current density of about 500 amp/sq ft at the hydrogen electrode. The permeability value obtained at Argonne differs widely from the value of 5.0×10^{-5} cc/(sq cm)(sec) at 550 C reported in the literature.⁴ The reason for this large discrepancy is not known. Evaluation studies are now being carried out on the other diaphragms received from Battelle Memorial Institute.

The possibility of achieving the desired current density at the hydrogen gas electrode by constructing an electrode with a large surface area has also been considered. Preliminary calculations (see ANL-6477, page 208), which were based on the utilization of 5-mil thick tubes ($\frac{1}{16}$ -in. OD)

⁴Schwartz, H. J., S. S. Carlton, and J. M. Fuscoe, ASD-TDR-62-18, April 1962, p. 32, Thompson Ramo Wooldridge, Inc., Cleveland, Ohio.

of pure iron for the construction of the electrode, indicated that the achievement of a suitable cathodic current density in a lithium hydride cell would require an electrode comprised of 3400 tubes arranged in a 10 x 30 x 30 cm bundle. Although the problems associated with the fabrication of this electrode could be solved, it was concluded that the expense and effort involved in such a venture were unwarranted until other avenues of research were more thoroughly investigated.

Some basic research is being carried out in support of the studies of the lithium hydride cell. Cooling-curve studies have been made

Figure V-5

PHASE DIAGRAM OF LITHIUM
HYDRIDE-LITHIUM CHLORIDE
SYSTEM

to delineate the phase diagram of the lithium hydride-lithium chloride system. The very reactive salts were weighed in a helium atmosphere glove box, which is described later in Section 3, and the experiments were conducted in a furnace well attached to the floor of the box. The furnace well was isolated from the rest of the system and the experiments were carried out in a hydrogen atmosphere in order to stabilize the lithium hydride. A eutectic melting at 494 C was found at 35 mole percent lithium hydride. The phase diagram of the lithium hydride-lithium chloride system is shown in Figure V-5.

2. Regenerative Bimetallic Cell Studies

Experiments with bimetallic cells were continued. These are concentration cells of the type

pure M_1 metal	ionic electrolyte containing ions of M_1 (valence Z_1)	M_1 dissolved in M_2 metal
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The emf of this cell is given by the equation

$$e = - \frac{RT}{Z_1 F} \ln a$$

where:

ϵ = electromotive force

Z_1 = valence of metal M_1 in ionic electrolyte

F = Faraday

a_1 = activity of M_1 in M_2

The overall cell reaction may be written as follows:

The study of bimetallic cells is being restricted to cells containing three liquid phases. A diagram of a bimetallic concentration cell is shown in Figure V-6. The advantages

Figure V-6
BIMETALLIC CON-
CENTRATION CELL

of cells of this type are their simplicity, low internal resistance, and ability to operate at very high current densities. This is in contrast to the lithium hydride cell in which the achievement of high current densities is the key problem. The regeneration of bimetallic cells, however, may prove to be considerably more difficult than the regeneration of the lithium hydride cell.

The current-voltage characteristics of six cells utilizing different bimetallic combinations were determined and are given in Table V-1. The lithium-bismuth cell was chosen for further study because of the high current density (450 amp/sq ft

at about 0.46 volt) produced in the cell and because the lithium-bismuth system presented fewer containment problems than some of the other cell systems, e.g., the lithium-tellurium system. The relationship between the saturated lithium-bismuth cell voltage and temperature is given by the following equation:

$$\epsilon = 0.4064 + 10.0212 \times 10^{-4} T - 7.8388 \times 10^{-7} T^2$$

The emf's of the lithium-bismuth bimetallic system as a function of temperature and composition are shown in Figure V-7. The liquid bismuth metal cathode saturated with lithium was operated against pure lithium anodes to obtain the lower emf-temperature plot shown in Figure V-7. The saturated lithium-bismuth electrode was then used as the anode and secondary standard electrode to obtain the other curves. Irreversible transfer of lithium in cells utilizing pure lithium anodes changed the composition of the cathode too rapidly to permit temperature cycling.

Table V-1

CHARACTERISTICS OF BIMETALLIC CELLS

System	Highest-Melting Intermetallic Compound	Melting Point of Highest Melting Compound (C)	Open-Circuit Voltage (volt)	Current Density at $\frac{1}{2}$ Open-Circuit Voltage (amp/sq ft)
Li-Te	Li ₂ Te	(unknown)	1.94	230
Li-Bi	Li ₃ Bi	1145	0.931	450
Li-Sn	Li ₇ Sn ₂	783	0.789	375
Li-Pb	Li ₁₀ Pb ₃	726	0.687	200
Li-Zn	Li ₂ Zn ₃	520	0.675	225
Li-Cd	LiCd	549	0.659	350

Figure V-7

CHARACTERISTICS OF LITHIUM-BISMUTH CELL

Smooth curves are computer derived least squares quadratic functions, σ = standard deviation, and X_{Li} = mole fraction of Li in Bi. Each curve includes about twenty data points at intervals of 50° or less.

In early studies, attempts were made to use the lithium chloride-potassium chloride eutectic as the electrolyte. It was found, however, that cell voltages became unstable at temperatures above 450 C. This instability was attributed to the reduction of potassium to the elemental metal by lithium. When the cell electrolyte was changed to the lithium chloride-lithium fluoride eutectic mixture, the voltages of the saturated lithium-bismuth cell remained stable at cell-operating temperatures as high as 825 C. Above this temperature, the cell voltages again became unstable. The reason for the instability above 825 C is not clearly understood. It is believed, however, that the instability is due to the rapid, irreversible transfer of lithium metal to the cathode. This transfer of metal may be caused by a considerable increase in the solubility of lithium in the fused salt electrolyte as the operating temperature of the cell is increased. That such an increase in solubility is likely is given credence by the work of Bredig *et al.*⁵ who found that the solubility of lithium metal in lithium chloride varies from 0.005 mole percent at 600 C to 0.02 mole percent at 1000 C.

Because of the instability of the cell voltage above 825 C and the relatively low emf-temperature coefficient of the cell, electrical regeneration of a cell using a pure lithium metal anode does not appear promising. It is possible, however, that these difficulties may be eliminated by using an anode of bismuth saturated with lithium (in equilibrium with solid Li_3Bi) and a cathode of bismuth containing about 0.01 to 0.05 mole fraction of lithium in bismuth. This cell would allow the use of many electrolytes which are not thermodynamically stable with respect to pure lithium and, therefore, it may be possible to find a lower melting mixture for use as the electrolyte. Moreover, it may be possible to operate the cell at higher temperatures and thus produce higher voltages. Both of these changes in operating conditions are made possible because of the lower activity of lithium in the anode.

Regeneration of the lithium-bismuth cell by means of a spontaneous thermal regeneration may also prove to be feasible. This method would involve raising the temperature of the lithium-bismuth alloy to an extent that would allow the separation of the lithium from the alloy by vaporization. By extrapolation of cell data from 825 C to 1000 C, it is possible to estimate the activity of lithium in the saturated lithium-bismuth cell at 1000 C. This value was estimated to be 2.4×10^{-2} . Since the vapor pressure of pure lithium at 1000 C is 40 mm Hg, the vapor pressure of lithium over a saturated lithium-bismuth alloy is about 0.8 mm Hg. By sweeping lithium with helium and condensing the vapor at a lower temperature, it may be possible to achieve thermal regeneration of the cell. The vapor pressure of pure bismuth at 1000 C is about 2 mm Hg. The activity of bismuth in the saturated lithium-bismuth alloy would have to be of the same order of magnitude as that of the lithium, if very little bismuth is to

⁵Dworkin, A. S., H. R. Bronstein and M. A. Bredig, *J. Phys. Chem.* **66**, 572 (1962).

appear in the gas phase. This is possible but is not known from experimental data at this time. Since the question of thermal regeneration cannot be settled completely by cell studies, it will be necessary to perform a transportation experiment at about 1000 C to determine the relative quantities of lithium and bismuth removed and their rates of removal in the vaporization process.

Although the calculations suggest that thermal regeneration of the lithium-bismuth cell is barely possible at 1000 C, it is likely that the chance of regeneration may be increased by using alkali metals heavier than lithium in the cell. These heavier alkali metals have greater vapor pressures and greater solubilities in their fused halide salts than does lithium. The disadvantage of the greater solubilities of the heavier alkali metals in the cell electrolyte may be offset by limiting the quantity of common ion halide salts in the cell electrolyte.

The availability of suitable materials of construction may very well become the overriding consideration in the selection of a cell for practical use. Very little data are available on the corrosion of structural materials by metals and fused salts at the high temperatures contemplated for the operation of the cell. In addition, corrosion data collected in stagnant systems may not be applicable to a circulating system. It is anticipated that a considerable research effort will be required in this area before the regenerative emf cell program can be successfully concluded.

3. Recirculating Helium Atmosphere Glove Box

The systems of interest in the regenerative emf cell program involve the use of fused salts and liquid metals that are not compatible with an ordinary atmosphere. An important development during the past year has been the design and construction of a recirculating helium atmosphere glove box. Prior to the completion of the box, experimental work was seriously compromised by contamination of the systems under study with impurities such as hydroxides, oxides, and nitrides. The helium atmosphere in the glove boxes (see Figure V-8) that are now being used contain less than 1 ppm water and 10 ppm oxygen and nitrogen. Experimental furnace wells have been attached to the metal floor of the glove boxes by means of water-cooled O-ring seals. These wells can be isolated from the rest of the glove-box system by an O-ring-sealed interior cap. Experiments may thus be set up in the furnace well in the purified helium atmosphere of the box; however, by placing the interior cap on the well, a high vacuum or other atmospheres may be maintained in the well during experimentation.

Figure V-8

RECIRCULATING HELIUM ATMOSPHERE GLOVE BOX

(Furnace wells are attached to the floor of the box. The helium purification system is located behind the glove box.)

B. Thermoelectricity Research

Studies in thermoelectricity were continued in an effort to contribute to the future technological development of direct conversion of nuclear reactor heat energy into electrical power by means of the thermocouple effect. An attractive feature of this method is the fact that the equipment needed for this conversion is simple and long lived.

1. Liquid Systems

The thermoelectrical properties of liquid systems are of importance since their study should contribute to the extension of solid state theory to the liquid state. Solid state investigations of the transport

properties of binary semiconductors are generally limited to very narrow composition ranges by virtue of narrow ranges of phase stability. Liquid binary systems offer a greater latitude for study of composition dependencies. At present there are only meager data in the literature on the electrical transport properties in such liquid systems, but a number of them have been shown to have semiconducting properties.

Preliminary work suggested that the study of binary systems from the indium-antimony-bismuth triad might be fruitful; therefore, binary systems of these elements were selected for the initial investigations. These elements are from a region of the periodic table in which solid state combinations have led to a number of semiconducting phases possessing interesting electrical properties. Two of these systems (indium-antimony and indium-bismuth) are iso-electronic and have electron-to-atom ratios which vary with composition. In the third system (antimony-bismuth), the electron-to-atom ratio is constant with composition. The study of these systems, therefore, should allow isolation of the effects that are directly related to the electron-to-atom ratios.

The furnace used in the experiment is shown in Figure V-9. The molten alloys are contained in a quartz-glass cell situated inside the H-shaped furnace. The two legs of the cell are joined by a cross piece. The voltages produced by maintaining the alloys at different temperatures in the two legs of the cell were measured by thermocouple electrodes of special construction. The difference in temperature of the alloys in the two legs was maintained at about 100 C during the runs. The H-shaped furnace, which is mounted on a pivot tube, can be rotated 180° for the purpose of emptying the quartz-glass cell at the conclusion of a series of experiments.

Sufficient information has been obtained in studies of the three systems to provide a tentative comparison of the systems. The results obtained with the antimony-bismuth system at a mean temperature of 750 C are shown in Figure V-10. The results of the indium-antimony and indium-bismuth systems are shown in Figures V-11 and V-12, respectively.

The antimony-bismuth alloys show a linear dependence of thermoelectric power on alloy composition. This behavior is attributed to the fact that the two elements may be considered to have the same outer electronic structure, and hence, no change in electronic structure occurs on alloying. On the other hand, the indium-antimony and indium-bismuth alloys show a complex relationship between thermoelectric power and alloy composition. This relationship, though complex, is remarkably similar for the two systems. The complexity of the relationship is attributed to the fact that the electronic structure does change with alloy composition in these systems since the outer electronic structure of indium

Figure V-9
H-SHAPED FURNACE USED IN THE STUDY OF
THERMOELECTRIC PROPERTIES OF
LIQUID ALLOYS

Figure V-10. ABSOLUTE SEEBECK COEFFICIENTS IN THE LIQUID SYSTEM ANTIMONY-BISMUTH AT 750 C.

Figure V-11. ABSOLUTE SEEBECK COEFFICIENTS IN THE LIQUID SYSTEM INDIUM-ANTIMONY AT 750 C.

Figure V-12. ABSOLUTE SEEBECK COEFFICIENTS IN THE LIQUID SYSTEM INDIUM-BISMUTH AT 450 C.

is different from the outer electronic structures of antimony and bismuth. The similarity of the two complex curves (Figures V-11 and V-12) is attributed to the similarity of the outer electronic structures of bismuth and antimony. All of the alloys were found to be distinctly more metallic in the liquid state than in the solid state.

2. Refractory Solid Thermocouple Systems

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 range. The uranium and thorium sulfide systems and their solid solutions have been selected for the initial studies.

Initial emphasis has been placed on thermoelectric power measurements. Measurements of the Seebeck coefficient as a function of temperature have been made on sintered specimens (~80 to 85 percent theoretical density) of uranium monosulfide, thorium monosulfide, and uranium sulfide-thorium sulfide solid solutions. The results, summarized in Figure V-13, show a decrease in Seebeck coefficient values with increasing thorium sulfide content. The trend in Seebeck coefficient values

Figure V-13

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

with composition appears to reflect the increased metallic nature of this system as the thorium sulfide content is increased. The trend is also consistent with room temperature resistivity values obtained on these specimens, namely, that the resistivity decreases with increasing thorium sulfide content, as shown in Table V-2.

Table V-2

ROOM-TEMPERATURE RESISTIVITY AS
A FUNCTION OF COMPOSITION FOR
US-ThS SYSTEM

Composition ^a (mole %)		Resistivity ($\mu\text{ohm-cm}$)
US	ThS	
100		405 ^b
75	25	395
50	50	250
25	75	175
	100	85

^aSintered specimens, about 85% theoretical density.

^bTentative value.

Measurements of the resistivity of uranium monosulfide as a function of temperature show that it increases but slightly with increasing temperature. A similar trend in resistivity with temperature has been reported⁶ for the refractory cerium sulfide system.

It can be concluded from the above thermoelectric parameter measurements that uranium sulfide, thorium sulfide, and their solid solutions are somewhat metallic.

Figure of merit* values for a sintered specimen of uranium monosulfide have been calculated. These values, which are tabulated below, were calculated using thermal conductivity values measured at Oak Ridge National Laboratory on a specimen supplied by Argonne.

⁶Ryan, F. M., I. N. Greenberg, F. L. Carter, and R. C. Miller, J. Appl. Phys. 33(3), 864 (March 1962).

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

Temp (C)	Thermal Conductivity [watts/(cm)(C)]	Figure of Merit (K ⁻¹)
40	0.0814	1.3×10^{-4}
75	0.0990	1.0×10^{-4}
125	0.0850	1.2×10^{-4}

These figure of merit values are roughly the same as the values found with the refractory cerium sulfide system in the same temperature range, and are approximately 5 to 10 times lower than the figure of merit values obtained with lead telluride (maximum operating temperature ~600 C).

The possibility of decreasing the carrier concentration of uranium monosulfide by the formation of solid solutions with suitable isomorphous compounds is currently being investigated as a means of enhancing the thermoelectric properties of uranium monosulfide.

VI. DETERMINATION OF NUCLEAR CONSTANTS

Calculations for reactor design and predictions of reactor behavior require neutron cross section data for fissionable and fertile materials, fission products, structural materials, and reactor poisons. Although a fairly complete body of information is available on cross sections of thermal neutrons, data on fast neutron cross sections are lacking for many nuclides of interest in fast reactor technology. To provide some of the needed data the Division is continuing its work in this field.

A. Determination of Fast Capture Cross Sections

Fast capture cross sections are being measured for the most part as a function of neutron energy. The target material is irradiated in a known flux of monoenergetic neutrons. The number of interaction events, such as capture, fission, and $(n, 2n)$, is determined by radiochemical separations and by absolute counting. The neutron sources for these measurements are the reaction $\text{Li}^7(p, n)\text{Be}^7$, produced by the bombardment of a lithium target with protons from a Van de Graaff accelerator and the fast flux of EBR-I. Neutrons with energies between about 0.1 and 2.2 Mev are made available by the Van de Graaff. This range of energies covers a large portion of the neutron energy spectrum found in fast reactors. Cross section experiments have also been carried out in the Transient Reactor Test Facility (TREAT) located at the National Reactor Testing Station in Idaho.

Fast Capture in Thorium-232

The fast neutron capture cross section of thorium-232 has been measured as a function of neutron energy in the range from 0.2 to 1.2 Mev. Thorium-232 is the fertile isotope in the uranium-233 reactor fuel cycle, and its capture cross section in this energy range is important in the estimation of the breeding ratio of this system. The presently available data¹⁻⁵ on the cross section of thorium show significant disagreement both in shape and absolute value.

In Figure VI-1, data from the literature are compared with data obtained at Argonne. Below 0.6 Mev, the agreement between the various data is satisfactory. Above 0.6 Mev the results of the present work are in qualitative agreement with other measurements, excepting the results of Hanna and Rose.¹ The work reported here indicates an increase in the capture cross section of thorium-232 in the vicinity of 0.8 Mev. This rise is in good

¹ Hanna, R. C. and Rose, B., J. Nuclear Energy **8**, 197 (1959).

² Staviskii, Yu. Ya. and Tolstikov, V. A., Atomnaya Energiya, **10**, 508 (1961)

³ Barry, J. F., O'Connor, L. P., and Perkin, J. L., Proc. Phys. Soc. **74**, 685 (1959).

⁴ Hughes, D. J., and Schwartz, R. B., Neutron Cross Sections, BNL-325, 2nd Edition (1958).

⁵ Lane, A. M., and Lynn, J. E., Proc. Phys. Soc. **A70**, 557 (1957).

agreement with the prediction of Lane and Lynn⁵ which considers only the competition of inelastic neutron scattering to the first two rotational levels of the thorium-232 nucleus. The qualitative effect of inelastic scattering to the next available residual nuclear states at about 0.8 Mev and 1.1 Mev will be a marked decrease in the capture cross section above the respective inelastic thresholds due to the increased number of channels from the compound nucleus.⁶ In the present experiment a decrease of this nature was noted in the values of the capture cross section of thorium-232 above about 0.8 Mev.

Figure VI-1

NEUTRON CAPTURE CROSS SECTION OF THORIUM-232

Fast Capture in Neptunium-237

Neutron capture by neptunium-237 produces the 2.1-day neptunium-238 whose gamma rays near 1.05 Mev can be used to measure its decay rate in the presence of both neptunium-237 daughters and small amounts of fission products. Relative cross sections obtained between 0.46 Mev and 1.3 Mev are shown in Figure VI-2.

⁶ Smith, A. B., *Phys. Rev.* 126, No. 2, 718 (1962).

Figure VI-2
RELATIVE NEUTRON ACTIVATION
CROSS SECTION OF NEPTUNIUM-237

Neutron Total Cross Section of Dysprosium

Measurements were made of the neutron total cross section of dysprosium between neutron energies of 13 and 210 kev. Preliminary results are shown in Figures VI-3 and VI-4. The standard deviations of the cross sections relative to each other are about ± 1.5 percent. This work is being continued to obtain data in the 1 to 2 Mev region.

Figure VI-3
NEUTRON TOTAL CROSS SECTION
OF DYSPROSIUM
(low range)

Figure VI-4
NEUTRON TOTAL
CROSS SECTION
OF DYSPROSIUM
(high range)

Rhodium-104m, 104

Several samples of rhodium were exposed in TREAT. The purpose of these tests was to determine the activation cross sections of the short-lived fission products rhodium-104, -104m by producing them in situ and observing the decay rate of rhodium-105 formed by the capture of a second neutron. This "double neutron capture" process occurs at a rate which depends on the square of the neutron flux. Since very rapid transients can be produced in TREAT, the instantaneous thermal neutron flux can exceed 10^{16} n/(sq cm)(sec). TREAT, therefore, offers promise of providing suitable conditions for double capture experiments in the case of nuclides which produce short-lived products upon capture of the first neutron.

Neutron capture by rhodium-103 produces both rhodium-104m and rhodium-104. Since both of these products are short lived, it is possible to measure the 36-hour rhodium-105 which forms when either rhodium-104m or rhodium-104 captures a second neutron. Several samples of rhodium exposed in the TREAT facility showed the presence of rhodium-105 when the gamma ray spectrum was analyzed. Since rhodium-105 can also result from neutron capture by ruthenium-104, the rhodium used in the TREAT experiments is being analyzed to determine the ruthenium level in the rhodium samples. The calculation of the double capture cross section of rhodium will be made when the results of the ruthenium analysis are completed.

B. Capture and Fission in EBR-I, Mark III

During the past year experimental capture cross sections (σ_c) and fission cross sections (σ_f) were determined for uranium-238, -235, and -233 and for plutonium-239 and -240 as a function of position in EBR-I, Mark III. About 70 sealed samples of high purity fissile and fertile isotopes were inserted in the reactor and subsequently analyzed. To obtain some of the data, special mass spectrometric techniques were needed to resolve the very small isotopic concentrations of the capture products from the principal isotopes one mass unit away. Improved mass spectrometric techniques developed at Argonne made it possible to measure the abundances of the capture nuclides to less than 2 ppm.*

The data are conveniently reported in terms of the defined ratio, alpha (σ_c/σ_f), for each isotope since this quantity is used directly for computation of the reactor breeding gain. The data presented here are a cross check against the reactor parameters which were predicted for EBR-I reactor in its design stages. The correlations of calculated with observed values are still in progress. Since the experimental alpha values were observed in samples that were essentially monoisotopic, extrapolations of these data to real reactor fuels composed of mixtures of isotopes in a similar spectrum is a simple matter of using weighted averages.

* The Chemical Engineering Division gratefully acknowledges the work of C. M. Stevens of the Chemistry Division for making the mass spectrometric measurements.

Capture and Fission Cross Sections of Uranium-238

The values of the capture and fission cross sections of uranium-238 in EBR-I, Mark III have been determined. These values and values of the ratio of capture to fission cross sections (α) are given in Table VI-1 for the vertical loading of samples in EBR-I and in Table VI-2 for the horizontal loading of the samples. The finite α values obtained reflect the high energy neutron spectrum of the reactor since α for U^{238} is infinite for slow neutrons.

Table VI-1

VERTICAL VARIATION OF ALPHA OF U^{238} IN EBR-I, MARK III

Reactor Position of Sample	Vertical Distance from Midplane (in.)	Capture (ppm of U^{238}) ^a	Fissions (ppm of U^{238})	Alpha (σ_c/σ_f)
upper blanket	9.86	26.7	2.88	9.27
upper blanket	7.86	42.3	6.96	6.08
upper blanket	5.86	61.0	19.8	3.08
core	3.87	69.7	69.8	0.999
core	1.87	75.7	110.0	0.688
core	-0.13	78.3	118.1	0.663
core	-2.12	-	106.4	-
core	-4.12	57.9	57.8	1.00
lower blanket	-6.11	43.4	16.6	2.61

^a Original U^{238} sample contained 100 ppm U^{235} and negligible amounts of other fissile isotopes.

Table VI-2

HORIZONTAL VARIATION OF ALPHA OF U^{238} IN EBR-I, MARK III

Reactor Position of Sample	Horizontal Distance from Reactor Axis (in.)	Capture (ppm of U^{238}) ^a	Fissions (ppm of U^{238})	Alpha (σ_c/σ_f)
core	0.93	78.3	118.1	0.663
core	3.80	75.4	65.7	1.15
inner blanket	4.60	58.9	29.0	2.03

^a Original U^{238} sample contained 100 ppm U^{235} and negligible amounts of other fissile isotopes.

Capture and Fission Cross Sections of Uranium-235

The variations of alpha for vertical and horizontal loadings of uranium-235 in EBR-I, Mark III are given in Table VI-3 and Table VI-4, respectively. These data are now available to reactor physicists.

Table VI-3

VERTICAL VARIATION OF ALPHA OF U^{235} IN EBR-I, MARK III

Reactor Position of Sample	Vertical Distance from Midplane (in.)	Capture (ppm) ^a	Fission (ppm) ^a	Alpha (σ_c/σ_f)
upper blanket	+10.14	40.1	170.3	0.235 ₅
upper blanket	+8.14	56.2	250.1	0.224 ₇
upper blanket	+6.14	74.4	384.1	0.193 ₇
core	+4.15	98.6	631.9	0.156 ₀
core	+2.15	113.3	885.3	0.128 ₀
core	+0.16	122.7	980.4	0.125 ₂
core	-1.84	112.7	901.8	0.125 ₀
core	-3.84	97.2	669.0	0.145 ₃
lower blanket	-5.83	74.0	388.7	0.190 ₄

^a Fissions or captures per 10^6 of U^{235} atoms.

Table VI-4

HORIZONTAL VARIATION OF U^{235} IN EBR-I, MARK III

Reactor Position of Sample	Horizontal Distance from Reactor Axis (in.)	Capture (ppm) ^a	Burnup (ppm) ^a	Alpha (σ_c/σ_f)
core	0.5	123.1	985.4	0.124 ₉
core	0.93	122.7	980.4	0.125 ₂
core	3.0	106.3	777.9	0.136 ₆
inner blanket	5.4	79.2	422.9	0.187 ₃
inner blanket	7.0	63.8	301.8	0.211 ₄

^a Fissions or captures per 10^6 of U^{235} atoms.

Fission and Capture Cross Sections of Uranium-233

The possibility of using thorium-232-uranium-233 as a fast breeder cycle has been considered for a number of years. The breeding ratio depends upon several factors: alpha, the ratio of capture to fission cross section of the fertile fuel, the number of neutrons produced per primary fissile species, the number of fertile atoms fissioned, and the number of neutrons produced per fission of the fertile species.

An experiment was performed to determine alpha for uranium-233. The uranium-233 used was of high isotopic purity (less than 4 ppm uranium-234) which was obtained through a joint effort with Oak Ridge National Laboratory. The number of captures in uranium-233 was measured by the mass spectrometric determination of uranium-234 and the number of fissions by the assay of cesium-137. In the calculation of the number of fissions, the half-life of cesium-137 was taken as 30.0 years, and its fission yield for the fast neutron spectrum as 6.51 percent. The values of the number of capture and fissions per million uranium-233 atoms, and the values of alpha are listed in Table VI-5 for the vertical loading in EBR-I, Mark III and in Table VI-6 for the horizontal loading.

Although the uranium-233 values were found to be generally lower than the corresponding values for plutonium-239, the values for the number of neutrons produced per fission is less for uranium-233 than for plutonium-239. It is believed, therefore, that the breeding ratio for uranium-233 will be somewhat less than the ratio for plutonium-239.

Table VI-5

VERTICAL VARIATION OF σ_c/σ_f OF U^{233} IN EBR-I, MARK III

Reactor Position of Sample	Vertical Distance from Midplane (in.)	Captures per 10^6 U^{233} atoms	Fissions per 10^6 U^{233} atoms	Alpha (σ_c/σ_f)
upper blanket	+9.82	25.9 ± 0.7	287.9	0.0900
upper blanket	+7.85	36.5 ± 0.8	416.7	0.0876
upper blanket	+5.90	47.3 ± 3	652.7	0.0725
core	+3.95	61.7 ± 3	1091	0.0566
core	+2.02	73.6 ± 2	1354	0.0546
core	+0.08	79.0 ± 2	1422	0.0556
core	-1.89	72.2 ± 1	1293	0.0558
core	-3.88	55.2 ± 2	877	0.0615
lower blanket	-5.88	41.7 ± 1	533	0.0782

Table VI-6

HORIZONTAL VARIATION OF σ_c/σ_f OF U^{233} IN EBR-I, MARK III.
MID-PLANE

Reactor Position of Sample	Horizontal Distance from Reactor Axis (in.)	Captures per 10^6 U^{233} atoms	Fissions per 10^6 U^{233} atoms	Alpha (σ_c/σ_f)
core	0.5	81.1 ± 3	1488	0.0545
core	1.25	79.0 ± 2	1422	0.0556
core	2.15	73.3 ± 3	1329	0.0552
core	3.00	66.6 ± 2	1189	0.0560
core	3.80	65.4 ± 3	1018	0.0642
inner blanket	4.60	55.5 ± 3	737.5	0.0753
inner blanket	5.40	48.4 ± 1	637.6	0.0759
inner blanket	6.20	43.5 ± 3	531.0	0.0819
inner blanket	7.00	36.6 ± 2	443.2	0.0826
outer blanket	10.3	22.6 ± 2	234.6	0.0963
outer blanket	12.3	19.7 ± 3	177.5	0.111
outer blanket	13.15	20.2 ± 2	168.3	0.120
outer blanket	14.05	23.8 ± 1	185.1	0.129
outer blanket	15.00	45.9 ± 2	368.5	0.125

Fission and Capture Cross Sections of Plutonium-239

Values of alpha for various positions of plutonium-239 in EBR-I, Mark III are shown in Tables VI-7 and VI-8. The values of alpha are somewhat greater than those for uranium-233 for samples having similar positions in the reactor.

Table VI-7

VERTICAL VARIATION OF Pu^{239} IN EBR-I, MARK III

Reactor Position of Sample	Vertical Distance from Midplane (in.)	Captures per 10^6 Pu^{239} atoms	Fissions per 10^6 Pu^{239} atoms	Alpha (σ_c/σ_f)
upper blanket	+10.13	47.6	306.2	0.155
upper blanket	+6.20	59.2	519.1	0.106
core	+4.27 ^a	68.8	799.3	0.0861
core	+2.31	78.3	1088.3	0.072 ₀
core	+0.41	87.5	1171.8	0.074 ₇
core	-1.56	79.1	1086.9	0.072 ₈
core	-3.54	65.8	756.2	0.087 ₀
lower blanket	-5.54	54.4	435.0	0.125

^a At edge of core and upper blanket.

Table VI-8

HORIZONTAL VARIATION OF Pu^{239} IN EBR-I, MARK III

Reactor Position of Sample	Horizontal Distance from Reactor Axis (in.)	Captures per 10^6 Pu^{239} atoms	Fissions per 10^6 Pu^{239} atoms	Alpha (σ_c/σ_f)
core	1.25	87.5	1171.8	0.074 ₇
core	2.15	81.4	1106.2	0.073 ₆
core	3.00	74.4	935.7	0.079 ₅

Plutonium-240 Capture in EBR-I, Mark III

Preliminary data on captures by plutonium-240 are given in Table VI-9. The values are for a horizontal loading of samples in EBR-I, Mark III.

Table VI-9

PLUTONIUM-240 CAPTURE IN EBR-I, MARK III

Reactor Position of Sample	Horizontal Distance from Reactor Axis (in.)	Captures per 10^6 Pu^{240} atoms
core	0.50	108
core	2.15	100
core	3.80	85
inner blanket	6.20	100

VII. ANALYTICAL CHEMISTRY

The Analytical Chemistry Group provides a broad spectrum of analytical support to the various groups of the Division. The work of the group includes "wet chemical" analyses, a wide variety of instrumental methods, radiochemistry, plutonium chemistry, gas chromatography, X-ray diffraction, and spectrometric analyses. During the past year more than 100 methods were employed to perform more than 12,000 analyses on 45 different elements. More than 600 X-ray diffraction patterns were determined for the identification of solid materials.

Research in analytical chemistry is, to a large extent, the outgrowth of the above service program. As the Division's program changes, existing analytical methods must either be modified or new methods developed to serve 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 one, and the analytical method must either tolerate or provide means for separating the constituent from as much as millionfold excess of such process materials as zinc, magnesium, salt fluxes, and aluminum oxide. Nearly 50 new analytical problems were undertaken and solved during the past year.

The development of methods for the determination of two fission product nuclides, technetium-99 ($t_{1/2} = 2 \times 10^5$ yr) and lanthanum-139 (stable), in both fissium and zinc-magnesium mixtures was necessary for the study of the behavior of these elements in the EBR-II fuel cycle and as a fission product monitor for fuel burnup in the EBR-II reactor. This study was carried out in cooperation with the ANL Idaho Division.

A. Methods for Determination of Burnup in the Fast Breeder Reactor, EBR-II

Of the 85 or so fission product nuclides which will be present in the discharged fuel, only technetium-99 and lanthanum-139 meet the many restrictive conditions which need to be imposed when selecting a fission product nuclide as a fission monitor. Neither technetium-99 nor lanthanum-139 is subject to decay corrections. Both nuclides are formed in high yield and are, therefore, relatively insensitive to the yield variations which occur with changes in the neutron energy spectrum. Moreover, technetium-99, lanthanum-139, or their precursors do not diffuse significantly in the fuel at the reactor's operating temperature of 650 C. At this temperature, cesium-137, the nuclide which has been used more frequently than any other for monitoring burnup in reactor fuels, diffuses out of the EBR-II fuel into the sodium bond. Neither technetium nor lanthanum is a constituent of the fresh uranium-fissium element

alloy which will be used as fuel in the EBR-II reactor. However, since technetium will be present in recycled fuel, the development of the lanthanum method becomes particularly important.

The amount of technetium-99 in the fuel is determined by chemical analysis. After dissolution of the sample, the technetium is separated from the other constituents of the fuel by distilling the volatile septoxide, Tc_2O_7 , from concentrated sulfuric acid. The amount of technetium in the distillate is determined spectrophotometrically after reaction of technetium with the chromogenic reagent, dithiol.

The technetium method has been tested on both synthetic samples of known composition and highly irradiated metallurgical test specimens. The precision of the analytical results on the synthetic samples was ± 0.7 percent relative standard deviation with no bias. The precision on the irradiated test specimens was ± 1.5 percent. Burnup values calculated from these data were in good agreement with values obtained by mass spectrometric uranium analysis. Burnup values obtained by cesium-137 analysis were found to be as much as 25 percent lower.

Lanthanum-139 is determined by isotopic dilution-mass spectrometric analysis. A known amount of lanthanum which is enriched to 13.5 percent in the lanthanum-138 isotope is added to an aliquot of the dissolved fuel specimen. The lanthanum is recovered by a series of solvent extraction and precipitation steps, and the isotopic composition of the purified lanthanum is determined mass spectrometrically. From the change in the lanthanum-138 to lanthanum-139 ratio, the amount of fission product lanthanum-139 can be calculated. (The amount of lanthanum-138 formed in the fission process is very small and, compared with the amount of lanthanum-138 added in the spike, is negligible.)

The lanthanum method has also been tested on both synthetic samples of known composition and highly irradiated metallurgical test specimens. The precision on the synthetic samples was ± 2 percent with no bias. The data available on the irradiated samples are not yet sufficient to firmly establish the precision and accuracy of the method when applied to irradiated fuels. However, burnup values obtained by the lanthanum method are in good agreement with values obtained by mass spectrometric uranium analyses.

In the table that follows, the burnup values obtained by the technetium-99 and lanthanum-139 methods are compared with the values obtained by mass spectrometric uranium analysis and by the cesium-137 method.

A COMPARISON OF BURNUP METHODS ON IRRADIATED METALLURGICAL TEST SPECIMENS

Sample No.	Uranium-235 Burnup, %			
	Mass Spec.	Cs ¹³⁷ ^a	Tc ⁹⁹	La ¹³⁹
1	1.39	1.04	1.49	1.35
2	1.58	1.41	1.68	1.56
3	1.52	1.32	1.66	1.46
Average Error, %	-	-16	+7	-3

^aThe lower values obtained with cesium as compared with technetium and lanthanum are attributed to the diffusion of cesium out of the EBR-II fuel and into the sodium in which the samples were irradiated. The samples were irradiated at 380 C; the reactor's operating temperature is about 650 C.

The small but significant differences that exist between the burnup values obtained by the technetium-99 and lanthanum-139 methods and the burnup values obtained by mass spectrometric uranium analysis are more probably attributable to errors in the fission yield values for these two nuclides than to errors in the lanthanum and technetium methods. Carefully prepared uranium samples are now undergoing special irradiations and will be used to remeasure the fission yields of these two nuclides.

Since most of the criteria that were used to select technetium-99 and lanthanum-139 as monitors for burnup in EBR-II fuel are common to all reactor systems, it is expected that these new methods of determining burnup will serve equally well for monitoring burnup in other reactor fuels.

B. Amperometric Titration of Uranium(IV) with Iron(III)

Amperometric endpoint detection has been incorporated in the titration of uranium(IV) with iron(III). This modification has produced gratifying results. After reduction by amalgamated zinc to a mixture of the (III) and (IV) oxidation states, the uranium is titrated first to the (III-IV) endpoint and then to the (IV-VI) endpoint. At 10 and 200 mg levels, relative standard deviations of 1 and 0.1 percent, respectively, are obtained.

C. Analyses of Trace Amounts of Thorium in Cerium Metal and Compounds

Separation by ion exchange and detection by neutron activation have been coupled for the determination of thorium in the range of parts per million in cerium metal and cerium compounds. Thorium is adsorbed on Dowex-1 anion resin from strong nitric acid and eluted with an ammonium nitrate-dilute nitric acid-ethylenediaminetetraacetic acid (EDTA) mixture. After brief irradiations in the CP-5 reactor, the 23-minute thorium-233 activation product is assayed by gamma spectrometry. Thorium at the 10 ppm level can be determined with a relative standard deviation of 10 percent.

D. X-ray Diffraction Studies of Scandium-Cadmium and Vanadium-Zinc Intermetallic Compounds

Measurements of the solubility of scandium in liquid cadmium led to the isolation and characterization of the intermetallic compound ScCd_3 . X-ray diffraction powder photographs of ScCd_3 can be indexed on the basis of a hexagonal unit cell with $a_0 = 6.324 \text{ \AA}$ and $c_0 = 4.853 \text{ \AA}$. The ScCd_3 structure can be referred to space group $D_{6h}^4 - P6_3/mmc$; structure type is Mg_3Cd (Do_{19}). The ScCd_3 structure may be described briefly as hexagonal close-packed as in the A3 type structure, but with the a-axes doubled. One atom in four of each of the layers at $z = 0$ and $z = 1/2$ is a scandium atom. Layers are arranged with respect to each other in such a manner that each scandium atom is in contact with three cadmium atoms in the adjacent layers.

A study of the vanadium-zinc system led to the isolation of two intermetallic compounds, VZn_3 and V_4Zn_5 . VZn_3 was characterized as having the common structure type $\text{AuCu}_3(\text{LiI}_2)$ in which $a_0 = 3.848 \text{ \AA}$. However, V_4Zn_5 appears to be nearly unique. The unit cell has eight vanadium and ten zinc atoms arranged in a body-centered tetragonal lattice whose dimensions are $a_0 = 8.910 \text{ \AA}$ and $c_0 = 3.227 \text{ \AA}$. The structure resembles that of Te_4Ti_5 . Atomic coordinates are in the process of being determined.

ADDENDUM

Publications

by

Chemical Engineering Division Personnel

(From January 1, 1962 to April 30, 1963)

A. Open-literature Publications

Baker, L., Jr. and R. Warchal

Studies of Metal-Water Reactions by the Exploding Wire Technique
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B. ANL Reports

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Foster, M. S., C. E. Johnson, and C. E. Crouthamel
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ANL-6531

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ANL-6522 (Classified)

Steindler, M. J.

Radiation Problems Associated with the Handling of the Actinide
Elements

ANL-6540

C. ANL Reports

Baker, L., Jr., and L. C. Just

Studies of Metal-Water Reactions at High Temperatures. III. Experimental and Theoretical Studies of the Zirconium-Water Reaction
ANL-6548

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Helium Purification Unit for High-Purity Inert-Atmosphere Boxes
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The Distillation of Uranium Hexafluoride and Bromine Pentafluoride in a 0.5-Inch-Diameter Packed Column
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Radiation Decomposition of Plutonium Hexafluoride

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Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride

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