ANL-7020

ANL-7020

MASTER

290
6-14-65

Argonne National Laboratory

CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1964 - April 1965

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Price \$6.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia.

ANL-7020
General, Miscellaneous,
and Progress Reports
(TID-4500, 39th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

CHEMICAL ENGINEERING DIVISION
RESEARCH HIGHLIGHTS

May 1964 - April 1965

R. C. Vogel, Division Director
M. Levenson, Associate Division Director
F. R. Masten, Assistant Division Director

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

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
GENERAL	1
I. COMPACT PYROCHEMICAL PROCESSES	3
A. EBR-II Fuel Cycle Development	5
1. Fuel Processing Facility for EBR-II	5
2. Skull Reclamation Process	16
3. Blanket Process	29
4. Purification of Argon From Nitrogen with Titanium Sponge	31
B. Processes for Fast Breeder Reactors Fuels	36
1. General Process Development	37
2. Separation of Fuel from Cladding	40
3. Distribution of Fuel Constituents between Liquid Metals and Molten Salts	41
4. Solubility of Uranium and Plutonium in Cadmium-Zinc- Magnesium Alloys	45
5. Solution Stability Tests	47
6. Processes for Oxide and Carbide Fuels	47
7. Halide Slagging of Uranium-Plutonium Alloys	47
8. Development of Engineering Equipment and Procedures for Molten Metal-Salt Extraction Operations	50
C. Supporting Chemical Studies	62
1. Chemistry of Molten Salts	62
2. Substitution of Cadmium and Magnesium for Zinc in U ₂ Zn ₁₇	64
3. Plutonium-Magnesium Phase Diagram	66
D. Supporting Engineering Studies	67
1. Determination of Critical Constants of Alkali Metals ..	67
2. Determination of Viscosities of Liquid Metals and Fused Salts	71
3. Measurement of the Surface Temperature of a Liquid Metal during Vaporization	72
E. Chemistry of Liquid Metals	72
1. Thermodynamic Studies	72
2. Liquid Sodium Chemistry	77
F. Preparation of Fuels for Fast Reactors	83
1. Solid Refractory Fuels	83
2. Studies of Mobile Blanket Fuels for Fast Reactors	94

TABLE OF CONTENTS

	<u>Page</u>
II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES	100
A. Laboratory Studies	101
1. Recovery of Plutonium from Alumina Bed Materials . .	103
2. Reaction of PuF_6 and Metal Fluorides	112
3. Behavior of Molybdenum in HF-O_2 and in Fluorine . . .	112
4. Fluorination of Plutonium-Containing Solid Wastes from Rocky Flats	114
B. Engineering - Scale Investigations	116
1. Processing of Nuclear Reactor Fuel of Low Enrichment	116
2. Reprocessing of Nuclear Reactor Fuels of High Enrichment	134
3. Corrosion Studies	145
4. Fundamental Fluidization Studies	147
III. HIGH TEMPERATURE REACTOR MATERIALS DEVELOPMENT	150
A. Current Status of High Temperature Phase Relations and Thermodynamic Properties in the Uranium-Uranium System	150
1. Objectives, Experimental Plans, and Recent Experimental Results	150
2. Development of Some Useful Theoretical Guidelines for Experimentation	153
B. The Uranium-Uranium System	159
1. Effusion Vapor Pressure Studies	159
2. Mass Spectrometric Effusion Studies	160
3. Transpiration Studies of Vaporization	160
4. Uranium-Uranium Phase Diagram Studies	161
C. Uranium-Uranium Monosulfide Phase Diagram Studies . . .	163
IV. CALORIMETRY	165
A. Fluorine Bomb Calorimetry	165
1. Two-Chambered Vessel	165
2. Single-Chambered Bomb	167
3. Fluorine Flow Calorimetry	170
B. Quartz-Crystal Thermometer	171
C. High Temperature Enthalpy Calorimetry	172
1. 1500°C Calorimeter	172
2. 2500°C Calorimeter	173

TABLE OF CONTENTS

	<u>Page</u>
V. REACTOR SAFETY	175
A. Metal-Water Reactions	175
1. Isothermal Reaction Rate Studies	175
2. Nonisothermal Reaction Studies	180
3. In-Pile Studies	184
4. Calculational Studies	189
B. Metal Oxidation and Ignition	192
C. Fast Reactor Safety Studies	195
1. Survey Study of the Chemical Interactions of Molten Sodium at High Temperatures with Fuel and Cladding Materials	195
2. Fuel Migration and Segregation in Mixed Uranium-Plutonium Compounds	195
3. Transient Boiling of Molten Sodium	197
4. Determination of High Temperature Physical Properties of Fast Reactor Materials	197
VI. ENERGY CONVERSION	198
A. Regenerative Emf Cells -- Physical-Chemical Laboratory Studies	198
1. Bimetallic Cell Studies: Lithium-Tin	199
2. Intermetallic Compounds and Alkali Metal in Fused Salts	200
3. Lithium Hydride-Alkali Halide Solid-Liquid Equilibrium	204
4. Regeneration Studies: Sodium-Bismuth	208
B. Regenerative Emf Cell -- Engineering Studies	211
1. Sodium-Bismuth "Open" Cell Studies	212
2. Sodium-Bismuth "Closed" Cell Studies	215
3. Engineering Material Corrosion Studies	216
4. Engineering Thermodynamic Studies	219
VII. DETERMINATION OF NUCLEAR CONSTANTS	226
A. Neutron Inelastic Scattering	226
B. Radiative Capture	228
C. Capture to Fission Ratios in EBR-II	230

TABLE OF CONTENTS

	<u>Page</u>
VIII. ANALYTICAL CHEMISTRY	231
A. Burnup Monitoring in Fast Reactors	231
1. Fission Yields of Molybdenum -95, -97, -98, and -100 . .	232
2. Fission Yields of Cerium-140 and -142	232
3. Fission Yields of the Ruthenium and Palladium Nuclides	232
B. Gas Chromatographic Analysis	233
C. X-ray Diffraction Studies of the Uranium-Zinc System, UZn _{8.5} to UZn ₁₂	233
D. X-ray Spectrochemical Analysis of Aluminum Oxide	234
E. Determination of Magnesium in a Number of Alloys	234
F. Electron Probe Microanalysis	235
IX. STUDIES AND EVALUATIONS	238
A. General Objectives	238
B. Cost Evaluation of Metal-Fueled Fast Reactors	238
1. Reference Compact Pyrochemical Process for Metal Fast Reactor Fuel	240
2. Preparation of Fuel for Processing	241
3. Removal of Fission Products	241
4. Partitioning of Uranium and Plutonium; Recovery of Uranium and Plutonium as Ingots of Metal	242
5. Composition of Recovered Uranium Ingots and Plutonium Ingots	243
6. Estimated Fuel Cycle Costs for the Argonne Reference Metal-Fueled Reactor	243
C. Divisional Study of Reprocessing of Fast Reactor Plutonium Fuels	245
1. Comparative Cost Analysis	246
2. The Cost-Throughput Relation for Reprocessing Plants: The Effect of Burnup	249
3. Shipping and Inventory Costs	250
4. Fuel Inventory Costs: Effect of Burnup and Out-of- Reactor Residence Time	254
ADDENDUM: Publications by Chemical Engineering Division Personnel from January 1, 1964, to April 30, 1965 . . .	257

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

GENERAL

The Chemical Engineering Division's program consists of work in the following areas: (1) development of processes and equipment for the recovery of fissionable and fertile materials from spent nuclear fuels, (2) development of methods for the synthesis and production of nuclear reactor fuels and materials, (3) studies of methods for the direct conversion of heat into electricity, (4) studies of the chemical and physical behavior of nuclear reactor fuels and materials suitable for use at high temperatures, (5) basic studies of unit operations in nonaqueous systems, (6) basic studies of the chemistry of substances that are of interest to nuclear technology, but which also provide fundamental data of importance to the scientific community, (7) studies of chemical reactions that are important to the safe handling of nuclear fuels and the safe operation of nuclear reactors, and the correlation of laboratory-derived data with conditions existing in nuclear reactors, (8) determination of nuclear constants, particularly neutron cross sections of elements that are of importance to the design and performance of fast breeder reactors, (9) study and evaluation of alternative methods for reprocessing of fast breeder reactor fuels, and (10) analytical chemistry in support of the research and development programs.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

I. COMPACT PYROCHEMICAL PROCESSES*

Compact pyrochemical processes have continued to be intensively developed for recovery and purification of refractory fuel materials discharged from power reactors. Because inorganic, radiation-stable materials are employed in these processes, they can accommodate short-cooled, high-burnup metal and ceramic fuels, thus permitting rapid recycle of fuel. The resulting reduction of fuel inventories outside the reactor is one of the major economic incentives for the development of these processes. This is an especially important factor for fast reactor fuels which contain a high concentration of valuable fissionable isotopes. Other advantages of these processes, which also have economic merit, are the avoidance or simplification of chemical conversions, small process volumes (and, hence, compact processing equipment), direct production of solid wastes, decrease in criticality problems because of the absence of aqueous solutions, and, in some of these processes, the retention of valuable alloying elements.

Because of the above characteristics, particularly the advantage of compact processing equipment, these pyrochemical processes are suited to use in small plants located on or near a reactor site. The concept of on-site recovery and recycle of discharged reactor fuel materials is being evaluated in Argonne's EBR-II reactor complex, which includes the EBR-II reactor and a spent-fuel processing and refabrication plant known as the EBR-II Fuel Cycle Facility. During the past year, the Facility was placed in operation and the first fuel material discharged from the reactor was successfully processed by melt refining** and fabricated into fuel elements for recycle to the reactor.

A scrap recovery process is under development for the recovery of the residue (skull) remaining in the melt refining crucible after the purified metal has been poured into a graphite mold in the melt refining process. The scrap recovery process is called the skull reclamation process. A blanket process for isolating plutonium bred in the blanket is also being developed for use in the EBR-II fuel cycle.

The EBR-II processes, which have been developed for a ^{235}U enriched metallic fuel, constitute the first generation of compact pyrochemical processes. Advanced processes for plutonium-bearing fast reactor fuels including ceramic (oxide, carbide, etc.) types also are under development. These advanced processes utilize molten metals and salts as processing media. Much of the technology required for the advanced processes has already been acquired in the development of the EBR-II processes. However, many new

* These processes have hitherto been called pyrometallurgical processes, but in order to convey better their applicability to ceramic fuels, such as oxides and carbides, and to emphasize the compact nature of these processes, they are now referred to as "compact pyrochemical" processes.

**See description of melt refining process in a footnote in Section IAla.

Figure I-1

EBR-II FUEL SUBASSEMBLY

Shown with component parts.
All dimensions in inches

EBR II FUEL ELEMENT

problems must also be solved, such as the separation of plutonium from rare and alkaline earth fission products (a problem not encountered with the enriched ^{235}U EBR-II fuel), chemical decladding of fuel, adaptations to ceramic fuels (e.g., oxide and carbide), evaluation of materials of construction, and development of engineering procedures for large-scale process applications.

A. EBR-II Fuel Cycle Development

1. Fuel Processing Facility for EBR-II

A fuel reprocessing-refabrication plant (Fuel Cycle Facility) is located adjacent to the EBR-II reactor. This arrangement not only permits the reactor to operate on a closed fuel cycle, but provides the Fuel Cycle Facility with short-cooled reactor fuel for demonstration of compact pyrochemical processes

Figure I-2

ISOMETRIC VIEW OF THE FUEL CYCLE FACILITY

The Fuel Cycle Facility is located adjacent to the EBR-II reactor building. Each fuel subassembly is transferred between the buildings in a shielded coffin via a passageway which terminates in the crane bay area. The subassembly is removed from or loaded into the coffin through an opening in the Air Cell floor. All mechanical operations in the cells are remotely performed by means of cranes, manipulators, pneumatic cylinders, and electric motors. These operations are viewed through 5-ft thick glass shielding windows in the cell walls. Operations in the Air Cell are observed and controlled from the operating annulus at three sides of the cell. Operations in the Argon Cell are viewed and controlled from either the operating annulus or the center control room. Service equipment which might become radioactive is installed in the shielded subcell area beneath the Argon Cell.

for a variety of fuel types (e.g., oxide, carbide, and metal). In the Fuel Cycle Facility, the processing equipment is contained in two heavily shielded cells, one with an air atmosphere (Air Cell) and the other with an argon atmosphere (Argon Cell). The cells are interconnected by means of vacuum locks which permit transfer of material while maintaining the integrity of the atmosphere in the Argon Cell.

Each partially spent fuel subassembly (Figure I-1) removed from the EBR-II reactor is transported in a shielded coffin to the Fuel Cycle Facility. There, the subassembly is dismantled, processed, refabricated, and then returned to the reactor. All process steps are carried out by remote means. Compact, pyrochemical processes are used for purifying the partially spent fuel. Figure I-2 is an isometric sectional view and Figure I-3 is a recent photograph of the Fuel Cycle Facility.

Figure I-3

RECENT PHOTOGRAPH OF THE EBR-II FUEL CYCLE FACILITY
WITH THE REACTOR PLANT IN THE BACKGROUND

The development of process equipment for the Fuel Cycle Facility has been a joint effort of the Central Shops Department, Reactor Engineering Division, Metallurgy Division, Remote Control Division, and Chemical Engineering Division. The locations in the cells where all major operations are performed are shown in Figure I-4. Actual installation of equipment items in the cells and all operations in the Fuel Cycle Facility are performed by members of the Idaho Division.

The Air Cell is used for operations which do not expose highly reactive or pyrophoric materials (sodium or fuel) to the cell atmosphere. These

Figure I-4

PROCESS EQUIPMENT LOCATION IN AIR CELL AND ARGON CELL

The floor plan shows the location of major equipment items in the process cells. A spent fuel subassembly is brought into the Air Cell through an opening in the cell floor. The subassembly is dismantled, and the fuel elements are transferred to the Argon Cell for processing. The fuel elements are decanned, chopped into short lengths, and charged to a melt refining furnace where all the fission products except the noble metals are largely removed from the fuel material. The refined metal is poured into a mold and the resulting ingot is charged to an injection casting furnace which produces fuel pin castings. These castings are removed from the molds and sheared to size, and the resulting fuel pins are inspected in the pin processing machines. Acceptable pins are inserted into sodium-loaded cans at the fuel assembly station and are then welded closed to complete the fuel elements. The fuel elements are transferred to the Air Cell, where they are leak tested, treated to establish a bond between sodium and metal, and then bond tested. Satisfactory fuel elements are assembled into a fuel subassembly, and the subassembly is loaded into a shielded coffin for return to the reactor.

operations include transfer of fuel subassemblies between the interbuilding transfer coffin and the Air Cell, dismantling of subassemblies containing fuel elements with partially spent fuel, testing of refabricated fuel elements, and assembly of the refabricated fuel elements into new fuel subassemblies.

The Argon Cell is used for operations that involve the handling of exposed reactive or pyrophoric materials. These operations include decanting of fuel elements containing partially spent fuel, purification of the fuel by melt refining, preparation of new fuel pins by injection casting, and assembly and welding of new fuel elements.

The Fuel Cycle Facility is operational and has been used to prepare subassemblies from unirradiated, enriched uranium-fissium. One irradiated core subassembly has been successfully processed to yield completed fuel elements.

a. Fuel Cycle Facility Operations

Testing and improving the processing and service equipment was continued.

Electromechanical Manipulators. The reliability of the electromechanical manipulators (two in the Air Cell and six in the Argon Cell) was increased by installation of a slip clutch in each hoist drive. This slip clutch protects the hoist mechanism and cables from damage due to overloads.

Shielding Windows. The shielding windows* in the cells were modified by mounting a 1/4-in. thick glass cover plate on the cell side of the window. This cover plate will protect the innermost 9-in. thick slab of shielding glass from bruising impacts, and the insulating effect of the 1/8-in. gas gap between the cover plate and the innermost shielding slab will result in an increased temperature of the slab when it is exposed to gamma irradiation. The protection from bruising impacts and the increased slab temperature will reduce the probability of damage to the innermost slab from spontaneous discharges of accumulated electrical charges. Such electrical charges result when thick glass slabs are exposed to intense gamma radiation.

* Each window consists of two remotely replaceable 9-in. thick glass slabs on the hot side of the cells and an oil-filled tank containing four 9-in. thick glass slabs. (Each end of the tank is sealed with a 1-in. thick glass cover plate.) A seal is made with a 1-in. thick glass pane located between the tank unit and the replaceable glass slabs. When the windows are not in use, they are further protected by steel shutters to reduce gamma darkening, thereby lengthening the useful lifetime of the windows.

Reclamation of Unirradiated Fuel Elements. Approximately 2500 fuel elements from the initial EBR-II core loading (enriched, unirradiated) were checked for sodium bonding, rebonded when necessary, and reassembled into subassemblies for future use in the reactor. Those fuel elements which were not successfully rebonded (about 10%) were decanned and reintroduced into the processing cycle. These process steps were performed in the cells. Operations with this large quantity of enriched material aided in familiarizing operating personnel with the required criticality control procedures.

Iodine Tracer Experiments. Radioiodine tracer experiments* have been performed to estimate the distribution of iodine which will be released during melt refining of irradiated fuel material. In one test, one curie of ^{131}I (as palladium iodide) was first added to 8300 g of uranium-fissium pins and the mixture was heated to 1400°C in a melt refining furnace.** The fume trap had been previously coated with sodium to simulate conditions which would result when melt refining sodium-bonded fuel pins. Most of the volatilized iodine was confined to the furnace; 0.1% escaped to the cell atmosphere and only trace quantities were detected in the off-gas system. The major concentrations of iodine in the off-gas system were 7×10^{-5} curie in an in-cell absorber-filter (a 2-in. layer of activated carbon followed by a filter with high efficiency for removing particulate matter) and 8×10^{-7} curie in the oil of a mechanical vacuum pump. The melt refining off-gas system is shown in Figure I-5.

Gas from the melt refining operation is stored in a 500-cu ft tank until atmospheric conditions permit its discharge. The tank is baffled and contains 1000 lb of activated carbon. After discharge from the tank, the gas passes through a heated silver nitrate tower for further removal of iodine, through high-efficiency filters, and then into a 70,000-cfm gas flow discharged to the atmosphere via a 200-ft stack. To test the iodine adsorption efficiency

* Performed by the Idaho Division.

** The melt refining furnace is heated inductively and is enclosed by a steel bell jar to permit the use of vacuum or a high-purity argon atmosphere. In the melt refining process, chopped, declad pins are charged to a zirconia crucible, liquated at 1400°C for about three hours under argon, and then poured into a mold. During melt refining, approximately two-thirds of the fission product elements are removed from the uranium by either volatilization or oxidation by the zirconia crucible. Most of the volatilized fission products other than krypton and xenon are collected by condensation on a Fiberfrax fume trap, which is inverted over the melt refining crucible. (Fiberfrax is a molded product of the Carborundum Corporation.) The oxidized fission products remain in the crucible as part of a residue (skull material), which is composed mainly of unpoured uranium metal and UO_2 . An auxiliary process utilizing liquid metal solvents (see EBR-II skull reclamation process) is employed to recover uranium from the skull material.

Figure I-5

OFF-GAS SYSTEM FOR MELT REFINING FURNACE AND OXIDATION FURNACE

Most of the fission products volatilized in the melt refining operation are sorbed on a Fiberfrax fume trap which rests on the crucible. Gas pumped from the melt refining furnace enclosure first passes through an in-cell filter where fission product vapors (including some iodine) are sorbed by a 2-in. layer of activated carbon, and particulates are removed on a high-efficiency glass-media filter. The gas then passes through a mechanical vacuum pump to a 500-cu ft baffled tank which contains 1000 lb of activated carbon in the first section. The pressure in the tank is maintained between 4 and 11 psia (atmospheric pressure is 12 psia). Periodically, when atmospheric conditions are favorable, gas is discharged from the tank. The discharged gas passes, in sequence, through a tower containing silver nitrate-coated packing maintained at 200°C for the removal of iodine, an exhaust pump, and a monitor to determine the xenon-133 concentration. The small gas flow (0.5 to 5 cfm) is then introduced into the building ventilation exhaust (30,000 cfm), and the mixture passes through high-efficiency filters. This gas flow then mixes with the ventilation exhaust from the neighboring buildings, and the total flow (70,000 cfm) is discharged to the atmosphere through a 200-ft stack. The flow entering the stack is continuously monitored for radioactive gases, radioactive particulates, and specifically for ^{131}I .

Gases from the oxidation furnaces pass through an in-cell filter identical to the filter previously described and into a 12-cu ft holdup tank. If radiation monitoring of the tank indicates low contamination of the gas in the holdup tank, this gas is then discharged into the building ventilation exhaust stream at times when atmospheric conditions are favorable. Otherwise, the gas is discharged from the 12-cu ft tank to the 500-cu ft tank in the melt-refining off-gas system.

of the carbon in the tank, one curie of ^{131}I was volatilized into the system at a point 50 ft upstream of the tank. The tank was then pumped out once each day for three days, being refilled with fresh argon immediately after each pump-out. Analysis of samples of the gas downstream of the tank showed that the total amount of iodine in the three discharges was 1×10^{-7} curie. The iodine retention was considered acceptable.

The crucible and skull from the iodine tracer experiment in the melt refining furnace contained approximately 30 millicuries of ^{131}I . The skull (see footnote in this section which describes melt refining) was oxidized in the skull oxidation furnace. No radioiodine was detected in the off-gas from this operation.

The ingot from the iodine tracer experiment in the melt refining furnace contained 70 microcuries of ^{131}I . The ingot was charged to an injection casting furnace, and pins were cast from the material. Analysis of the cast pins and the heel remaining in the furnace showed essentially the same concentration of ^{131}I as had existed in the charged ingot. Approximately one microcurie of ^{131}I was detected in the oil of the vacuum pump for the injection casting furnace. An off-gas filter, similar to the in-cell filter used for the melt refining furnace, has since been installed in the off-gas line from the injection casting furnace to reduce the possibility of release of iodine to the atmosphere.

Processing of Irradiated EBR-II Fuel. In August, 1964, one core subassembly and one blanket subassembly were transferred from the EBR-II reactor to the Fuel Cycle Facility. The core subassembly had 0.1 a/o burnup. Immediately following the transfer of these subassemblies, the reactor became inoperative owing to mechanical difficulties, and no further subassemblies have been transferred.

Each of the irradiated subassemblies was transferred from the reactor to the Fuel Cycle Facility in the interbuilding coffin, and the adhering sodium was removed from the subassembly while it was in the coffin. The sodium removal procedure involves the slow oxidation of sodium and the removal of the oxide and hydroxide by a water wash. Previous tests with sodium-coated, unirradiated subassemblies had shown that essentially all of the sodium (30 to 40 g) adhering to a subassembly was reacted by the procedure and that greater than 90% of the oxide (or hydroxide) was removed by water wash. The sodium removal step proceeded satisfactorily with the irradiated subassemblies. The fuel and blanket elements, inspected after disassembly of each subassembly, appeared to be clean.

Eighty fuel elements from the irradiated core subassembly were decanned, chopped, and transferred to the melt refining furnace for processing. The pouring yield from the melt refining operation was 92.7% (the charge was 5.4 kg fuel pins and 2.9 kg enriched scrap). The removal of cerium and

volatile fission products was 99% or greater. These removals are in good agreement with the results from small-scale experiments*. Retention of iodine in the ingot amounted to 0.1% of the iodine in the charge. This is appreciably greater than the retention experienced (0.007%) in the radioiodine tracer run.

The skull remaining in the melt refining crucible was oxidized in the skull oxidation furnace. The skull charge weight was 632 g and the weight of the oxidized product indicated complete conversion to U_3O_8 . Iodine was not detected in the off-gas from the skull oxidation furnace.

The ingot resulting from the melt refining run was charged to the injection casting furnace and cast into fuel pins. Less than 0.01% of the iodine in the ingot was found in the off-gas vacuum pump oil and less than $10^{-5}\%$ was found in the off-gas beyond the vacuum pump.

The operations with this irradiated material showed no unexpected spread of radioactive contamination. Minor remote clean-up operations in the Air Cell, after disassembly of the fuel subassembly, reduced the contamination in the Air Cell to a level which permitted personnel entry. As expected, the operations in the Argon Cell caused widespread surface contamination in that cell. The transfer of fission products (particularly ^{131}I) to the off-gas from the melt refining, skull oxidation, and injection casting furnaces was not greater than anticipated. Although the results from processing a single irradiated fuel subassembly are inadequate to predict the spread of contamination from routine processing of irradiated fuel material, these results are encouraging.

b. Argon Cell Atmosphere

Because highly reactive fuel and scrap fuel materials are handled in the Argon Cell of the Fuel Cycle Facility, low concentrations of oxygen and water vapor are maintained in the atmosphere in the cell. The potentially high concentration of volatile fission products in the Argon Cell atmosphere makes it desirable to operate the cell at a pressure lower than the pressure in the surrounding areas. Oxygen and water vapor are removed from the argon atmosphere by a purification system which includes a compressor, a catalyst (palladium) bed, and a desiccant bed (Linde 5A Molecular Sieves). In the catalyst bed, the oxygen is catalytically reacted with added hydrogen to form water vapor. The water vapor formed by the catalytic reaction and the water vapor present in the argon atmosphere are removed by the desiccant bed.

The Argon Cell was operated from August 1963 to February 1964

* The removal of zirconium amounted to 50%, which is higher than that experienced in small-scale experiments. Zirconium removal will be followed in subsequent melt refining processing of other spent irradiated core subassemblies to determine if the same high removal continues to be experienced.

with an argon atmosphere. During February 1964 the Argon Cell was filled with air to facilitate maintenance of cranes and manipulators, to speed installation of additional equipment, and to remove mercury which had spilled into the cell from a seal located near the cell ceiling. In late February 1964, the cell was refilled with argon and has since been operating with an argon atmosphere.

The Argon Cell is being maintained at a negative pressure of 3 in. of water. The rate of air in-leakage has been 0.003 to 0.005 scfm with occasional higher rates which have been traced to leaks in transfer lock gas-kets or process equipment piping. It was determined that water vapor and oxygen concentrations as low as 5 ppm and 8 ppm, respectively, could be maintained in the cell. During operation at these low water vapor and oxygen levels, difficulties were experienced in the operation of the equipment used to remove cladding from fuel elements. These difficulties were attributed to sodium wetting of metal parts which occurs at low levels of water vapor and oxygen. Separate investigations had shown that such low concentrations caused rapid wear of graphite bearings and motor brushes. To avoid these difficulties, it was decided to operate the Argon Cell with water vapor and oxygen concentrations each between 20 and 60 ppm. To permit separate control of each impurity, a valve was installed to bypass the desiccant bed. The oxygen and water impurities are separately controlled as follows: (1) by adding hydrogen and bypassing the desiccant bed, elemental oxygen, is removed by being catalytically converted to water vapor; and (2) by not adding hydrogen and by passing the cell gas through the catalyst bed and desiccant bed, water vapor alone is removed. The Argon Cell has been maintained at these higher water vapor and oxygen concentrations since July 1964, and the increase does not appear to be detrimental to fuel processing and has apparently reduced sodium wetting and brush wear.

The nitrogen concentration in the cell atmosphere is not directly controlled but is maintained at a low percentage by the purging action of normal cell operations. Cell gas is removed in the operation of transfer locks and enclosed furnaces, and high-purity argon is automatically added to the cell to maintain a constant pressure in the cell. The nitrogen concentration in the cell atmosphere has been approximately six percent for the past six months. Because future compact pyrochemical processes may require nitrogen concentrations substantially below six percent, nitrogen removal by chemical gettering is being investigated (see section IA4).

Carbon dioxide is introduced into the Argon Cell with inleaking air and from the photolytic and radiolytic decomposition of organic materials in the cell. This contaminant, which is known to react with fuel materials, is not removed from the cell atmosphere by the purification system because the CO_2 which initially sorbs on water-free desiccant material is desorbed as the desiccant sorbs water. Samples of gas taken from the Argon Cell in

late 1964 showed 74 ppm CO_2 .^{*} The CO_2 in the cell atmosphere was reduced from 74 to 24 ppm by passing two cell volumes of gas through a freshly regenerated desiccant bed. The desiccant was then again regenerated to remove the sorbed CO_2 . This procedure will be used periodically to control the CO_2 concentration in the Argon Cell.

In 1963 the original catalyst (palladium) became poisoned, presumably due to mercury which had been spilled in the Argon Cell (see ANL-6900, pp. 100-103). This catalyst was replaced in February 1964. Soon after the replacement, samples of the catalyst taken from the top (inlet side) of the bed showed that the thin active layer of catalyst on the pellets was being eroded away from the inert ceramic carrier. Experiments^{**} with a model bed using the 1/8-in. right cylinder pellets showed that the pellets in the upper portion of the bed could move about vigorously due to vortex shedding^{***} and the erosion was first attributed to this movement. However, further experiments with the model bed showed that the average velocity in the catalyst bed was too low to cause particle movement by vortex shedding and that particle movement was probably caused by the high velocity in the plume from the inlet pipe. The upper section of the catalyst vessel has been packed with stainless steel wool, and this baffling appears to have stopped the particle movement.

It has become evident from experience in the Argon Cell that there are a number of problems uniquely associated with the operation of equipment in a dry argon environment. The lubricating and wetting properties of certain materials are changed markedly when their environment is changed from moist air to very dry argon. Heat transfer rates for natural or forced convection, under otherwise identical conditions, are less in argon than in air. The electrical insulating strength of argon is much less than that of air. These and other properties of the gaseous environment greatly affect equipment performance.

To investigate these effects, an argon-atmosphere environment system has been designed and constructed by the Chemical Engineering Division. The system includes two conventional gloveboxes, a large enclosure, and a purification system. The gloveboxes are being used for the development of equipment and for testing the operation of component parts. The large enclosure (24 ft long, 12 ft wide, 14 ft high) will be used for the operation of prototype equipment designed for use in the Fuel Cycle Facility Argon Cell or

* The CO_2 concentration was determined by condensing the CO_2 , at liquid argon temperature, from a large volume of cell gas and then evaporating the CO_2 into a small volume of carrier gas for chromatographic analysis.

** Performed by the Idaho Division.

***In the flow of a fluid past an object, fluid vortices are shed periodically downstream from the object. This results in a periodic force on the object, perpendicular to the direction of flow (see R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, eds., Chemical Engineers' Handbook, 4th Ed., McGraw-Hill Book Co., Inc., 1963, Section 5, p. 53).

Figure I-6

INTERIOR OF LARGE ARGON-ATMOSPHERE ENCLOSURE

Equipment will be operated in an argon atmosphere in this large enclosure (24 ft long, 12 ft wide, and 14 ft high) to determine environmental effects on equipment performance. Manipulations will be performed with a crane or through gloves mounted in 29 windows in the cell walls. The crane is supplied power from a variable-frequency generator to permit continuously variable speed control. Fluorescent fixtures are mounted above three of the ten roof windows to provide lighting. Three 3-ton capacity refrigerated cooling units are provided for heat removal; two are shown above windows in the right-hand wall. A skull reclamation furnace is seen in the rear, with agitator and transfer line installed. The crane is lowering a funnel into the furnace charging chute. A skull oxidation furnace, in the right foreground, will be used to prepare uranium oxide for tests of the skull reclamation process. Services for the furnaces are provided through service ports located below the windows in the cell walls.

similar cells with an argon atmosphere. The interior of the large enclosure is shown in Figure I-6. The purification system is very similar to that used for the Argon Cell and utilizes prototype equipment which was used in the development of the Argon Cell purification system.

It is anticipated that the use of the gloveboxes and the large argon-atmosphere enclosure will permit the detection of environmental effects upon equipment and processes in the design and prototype stages. Such early detection should reduce failures in subsequent plant operations of equipment or processes.

2. Skull Reclamation Process

The skull reclamation process is an adjunct to the melt refining process in the EBR-II fuel cycle and has been developed to recover uranium from melt refining crucible residues for return to the main fuel stream. These residues, also known as skulls, consist principally of unpoured metal, some oxidized uranium, and oxidized rare earth and alkaline earth fission products that are concentrated in the skull material during melt refining. The recovery process must effect a separation of uranium from the rare earth and alkaline earth metals and also from noble and refractory metal fission products (Zr, Mo, Ru, Pd, Nb, and Tc) that are not removed in melt refining. The removal of these elements in the skull reclamation process offsets their generation by fission of uranium in the reactor and serves to maintain their concentrations at nearly constant values in recycled fuel.

A flowsheet of the skull reclamation process is presented in Figure I-7. The flowsheet differs from the presented previously (ANL-6875, p. 17) only in the final step, which is now performed in a tungsten rather than a beryllia crucible. This change of the retorting crucible material prohibits melting of the recovered uranium in the retort after solvent evaporation because tungsten is fairly soluble in molten uranium (~1%). The retort cake is now hydrided to loosen it from the crucible. At this point a number of alternative procedures exist. The hydride may or may not be dehydrided in the tungsten crucible. Either the hydride powder or uranium metal powder may be returned directly to the main fuel stream by way of the melt refining step, or, before return to melt refining, either may be consolidated into an ingot in a beryllia crucible. If the hydride is returned to the stream, dehydriding occurs as it is heated in the melt refining or beryllia crucible. The method chosen will depend upon experience gained in the handling of these powders.

a. Pilot Plant Operation

Demonstration of the skull reclamation process on an engineering scale of 1.5 kg of uranium has continued during the past year. There has been a steady evolution of techniques and equipment. The current series of runs is expected to demonstrate the reliability of the process and will terminate this phase of the development.

Figure I-7

FLOWSHEET FOR SKULL RECLAMATION PROCESS

*The uranium hydride product may be decomposed and consolidated into a metal button in a beryllia crucible for return to melt refining, or it may be returned directly to melt refining.

A cross-sectional view of the furnace assembly employed in the pilot-plant demonstration was presented previously (ANL-6875, p. 21). The salt and metal solutions are contained in a tungsten crucible which is located inside a graphite secondary that also serves as a susceptor for induction heating. A bell jar enclosure is provided for the crucible, insulation, and heating coils. The enclosure is required for maintenance of a high-purity inert gas atmosphere and to permit pressurization of the furnace when it is desired to transfer molten metals or salts out of the reaction crucible through a transfer line. The bell jar contains three nozzles, one of which is used for an agitator; the other two are used as need requires for looking into the furnace, for addition of reagents, and for insertion of solution transfer lines, sampling tubes, liquid level probes, and thermocouples. The bell jar furnace is located in a glovebox (see ANL-6766, p.26) which has been enclosed during the past year and which now contains a dry, nitrogen atmosphere ($\sim 93\% \text{N}_2$, $6\% \text{Ar}$, $0.5\% \text{O}_2$, and $2.5 \text{ ppm H}_2\text{O}$).

During the past year, 18 runs (SKR-9 through SKR-26) were started in the pilot plant. All but three of these runs (SKR-10, -18, and -22) were completed through the preparation of a product solution. About one-half of the product solutions have been retorted to yield a uranium metal product. The retorting has been performed in a second furnace which was completed since the last report. This furnace, located in a glovebox as shown in Figure I-8, has the same general design as a larger furnace shown in this report in Fig. I-14. The retort is a vertical assembly consisting of an evaporator and a condenser-condensate receiver unit. This assembly fits within a melt refining bell jar furnace, and may be interchanged with melt refining equipment for realloying of recovered skull material into new fuel alloys. The glovebox contains an argon atmosphere to prevent oxidation of the finely divided uranium product during handling at the conclusion of a run.

Equipment Performance

Tungsten Crucibles. Three pressed-and-sintered tungsten crucibles, each with an internal diameter of approximately 10 in., have been fabricated for the pilot plant runs. The first of these was a manufacturing reject which was later repaired by having a coating of tungsten plasma-sprayed on the exterior surfaces. This crucible is still in service and has been used for many runs (SKR-11 through 18), and for remelting 48 waste ingots for sampling. The second crucible was employed in all the early shakedown operations and for the first ten demonstration runs, but cracked during run SKR-10. After the intermetallic decomposition step of that run, a large melt of a near-eutectic, 50 w/o Zn-50 w/o Mg solution (melting point $\sim 350^\circ\text{C}$) and flux (solidus $\sim 560^\circ\text{C}$) was frozen and then remelted. (In the normal processing sequence, this melt would not be frozen.) As a result of expansion of the metal phase during melting, which expansion may have been partially restrained by the still-frozen flux, severe stresses were created, causing the crucible to crack. Remelting of the eutectic magnesium-zinc alloy is to be avoided because its melting

Figure I-8

SMALL-SCALE RETORTING EQUIPMENT

The equipment shown installed within a melt refining furnace is interchangeable with melt refining equipment. The bell jar is shown in the up-position.

point of about 350°C lies near and possibly below the brittle-to-ductile transition temperature of tungsten, which is between 150°C and 450°C depending on the degree of working. Since this crucible failed, freezing of the alloy in the tungsten crucible has been avoided, even when there have been equipment difficulties, either by maintaining the alloy temperature above the melting point or by transferring the melt from the crucible. The third pressed-and-sintered crucible was first employed in Run SKR-23 and has since been used without incident in four runs.

When used properly, pressed-and-sintered tungsten crucibles have given very good performance. However, such crucibles are fairly

expensive, and because of the inherently thick walls required for the pressing operation, they are heavy and unwieldy. Alternative methods of fabrication which may result in lighter crucibles are being evaluated. A welded tungsten crucible was successfully employed in Runs SKR-19 through 21, but cracked and leaked in Run SKR-22. The welds in this crucible had not fully penetrated the base metal, thereby providing notches for initiation of cracks. Any welded crucible will contain a weld-affected zone having structural properties inferior to those of the surrounding metal. Use of a welded tungsten crucible will be considered further when significant improvements are made in tungsten welding techniques.

Process Performance

The requirements of the skull reclamation process are moderate. Since only 5 to 10% of the fuel is handled in the skull reclamation process, a uranium recovery of 95% is adequate and results in an overall uranium recovery of 99.5% or greater. The required removal of fission products is dependent upon the fuel burnup and the fraction of the total fuel which is directed to the skull reclamation process; in general, fission product removals of between 60 and 90% will suffice to maintain proper fission product concentrations in the recycled fuel. These recovery and purification goals have been shown to be achievable by pilot plant runs made to date. Because about 10% of the product solution remains in the processing crucible as a heel which is to be recycled, uranium recovery in individual runs has been inferred from cumulative losses. These heels are being recycled in the current series of reliability runs, and it is expected that uranium recoveries greater than 95% will be demonstrated. Fission product removals have been as follows: alkali and alkaline earths, > 99%; rare earths, > 90%; ruthenium and molybdenum, > 80%; and zirconium, > 75%. These removals meet process requirements. The performance of individual steps (Fig. I-7) is summarized below.

Extraction of Noble and Refractory Metals. In the extraction step for the removal of noble and refractory metals, the metallic uranium present in the recycled heel from the product solution is oxidized into the skull oxide-bearing flux phase by zinc chloride. The refractory and noble metal fission products and alloying elements are extracted into the waste zinc phase, appearing either in solution or in suspension. Since volatilization of zinc chloride has been a problem, it has been expedient in some runs to lower the operating temperature from 800°C to 700°C for this step. Although the reactions appear to be rapid at 700°C, the experience at the lower operating temperature is as yet insufficient to warrant a definite change in the operating temperature.

The waste metal is transferred from beneath frozen flux at 525°C. This transfer has proved efficient in removing insoluble ruthenium and molybdenum if the metal is agitated at a moderate rate (~400 rpm) during the transfer. A phase transfer efficiency of about 93% is typical in this step. The corresponding noble metal removal has been in excess of 80%. Of the uranium

charged in this step, about 0.3% was transferred with the zinc phase; although this is a low value, it is somewhat higher than expected.

Uranium Reduction. In the uranium reduction step, oxides of uranium, zirconium, and rare earths suspended in the flux are reduced by magnesium and extracted into the zinc-magnesium phase. The alkaline earths and alkali metals are not reduced and remain in the flux. The reduction of zirconium must be efficient in this step in order to ensure its removal in the succeeding step. (Zirconium is removed in the supernatant phase after crystallization of a uranium-zinc intermetallic compound.)

Reductions to both uranium and zirconium metal proceed well at 800°C. Typical uranium reductions are 99.5% complete and appear to be limited to this value by chemical equilibrium.

Intermetallic Compound Precipitation. By cooling the system to 525°C, uranium is crystallized as an intermetallic compound with zinc. All but about 0.6% of the uranium precipitates at this temperature. Most of the zirconium remains in solution in the supernatant metal liquid, but 8 to 12% of the zirconium coprecipitates with the uranium-zinc intermetallic compound. Most of the supernatant zinc solution is transferred out of the crucible at 525°C, leaving behind the intermetallic precipitate and the flux (which is frozen at 525°C). A typical phase transfer of 85% of the supernatant phase removes about 75% of the zirconium. Transfer of greater than 0.5% of the uranium has resulted by entrainment of crystals of the intermetallic compound in the supernatant phase as it is being transferred. In several runs, considerable transfer of uranium by entrainment occurred. This is undesirable, but by careful control of the operating variables, and particularly by elimination of backflushing of argon gas through the transfer line during the final stages of uranium-zinc intermetallic precipitation, the uranium entrainment can be kept below about 1% in this step.

Decomposition Step. After the intermetallic precipitation step, the major contaminants associated with the uranium are the rare earths, which coprecipitate almost completely with the uranium-zinc intermetallic compound. The addition of magnesium to the precipitate in an amount equal in weight to the zinc in the remaining supernatant solution results in decomposition of the intermetallic compound, with subsequent precipitation of metallic uranium and dissolution of the rare earths. The decomposition is performed at 700°C to insure melting of the magnesium (m.p. 650°C) and hence rapid alloying between zinc and magnesium. The rare earths distribute about equally between the 50 w/o Mg-50 w/o Zn solution and the flux. The crucible is then cooled to 450°C to reduce the uranium solubility in the metal phase to about 0.1 w/o, and the metal is transferred to waste. The crucible contents are then reheated to about 700°C, and the flux is also transferred to a waste container. Phase transfers in excess of 90% for the metal and flux wastes can be expected. About 1% of the uranium is found in the metal waste and about 0.5% in the flux

waste. These losses are approximately the solubility and chemical equilibrium values.

Product Dissolution. The uranium precipitate remaining in the crucible is redissolved in a 14 w/o magnesium-zinc solution, in which uranium has an appreciable solubility (up to 20 w/o at 800°C). About 90% of the final product solution, a 12 w/o uranium-12 w/o magnesium-zinc solution, is then transferred to a mold. The balance of the solution is recycled to the next run. The product ingot is later retorted for isolation of a uranium metal product. The total time required from the charging of skull oxide to the transfer of the product solution is about 18 hr.

Retorting. The product solution ingot is charged to a tungsten crucible, and the magnesium and zinc are evaporated off under vacuum. The maximum temperature of the retort crucible is restricted to 950°C to avoid interaction of tungsten and uranium. When the evaporation is finished, the uranium is hydrided at about 300°C under a hydrogen pressure of one atmosphere. This frees the uranium sponge from the crucible (to which it frequently adheres) and converts it to a powder, which may be easily removed and handled. The uranium can be dehydrided in place by raising the temperature to about 400°C and reducing the pressure, or it can be removed and charged as the hydride to melt refining along with discharged fuel material. Both procedures have been employed and are being evaluated. The recovery of uranium from the retort is essentially quantitative. Entrainment losses of uranium in the condensate have been less than 0.1%.

Realloying. A retorted product (957 g) from a pilot plant run has been combined with a charge of uranium-fissium pins (9050 g) and melt refined in order to test the realloying of reprocessed skull material with fuel pins as is proposed for the EBR-II fuel cycle. An excellent pouring yield of 93% was attained in the run, and no difficulty was evident in achieving a satisfactory blend of the two materials. More runs of this type are planned.

Other Process Considerations

Control of Fumes. At the maximum operating temperatures in the process there is an appreciable vapor pressure of zinc (~230 mm Hg at 800°C),* magnesium (~25 mm Hg at 800°C), zinc chloride (470 mm Hg at 700°C), and magnesium chloride (~2 mm Hg at 800°C). The amount of metal vaporized from the reaction crucible is generally small, because of the overlying flux layer, but some vaporization of salts occurs, particularly under certain conditions with zinc chloride. The use of fume traps at the top of the crucible has been tried with little success to date, but the continued development of fume traps for plant operation is advisable.

* The vapor pressures of these elements over the melts are somewhat less than these values, which are for pure liquids.

Metal fuming has been more of a problem at the conclusion of a phase transfer when the pressurizing gas is vented through the transfer line into the transfer receiver. Containment of metal fumes in a transfer receiver has been effected by means of a resin-impregnated fiberglass filter fitted as a cover on the transfer receiver.

Flux Preparation. The flux (47.5 m/o MgCl_2 , 47.5 m/o CaCl_2 , 5 m/o CaF_2) used in the skull reclamation process must be pretreated to remove residual moisture. The most difficult constituent to dry is MgCl_2 , which reacts with moisture to form MgOHCl or MgO and HCl gas. In several runs, the residual MgOHCl reacted with magnesium from the Mg-Zn solution in the reduction step to produce MgO , MgCl_2 , and hydrogen. The hydrogen gas bubbling up from the bottom of the salt caused foaming of flux out of the crucible.

All of the MgCl_2 and CaCl_2 is now first mixed and then pretreated with magnesium prior to use. Since magnesium floats on the salt, the hydrogen formed does not cause foaming. The magnesium oxide produced in the flux by the decomposition of MgOHCl is not a problem in the skull reclamation process and could be filtered out if this were deemed desirable. The calcium fluoride is sufficiently dry as received and is subsequently added to the pretreated MgCl_2 - CaCl_2 flux.

Zinc chloride is the most hygroscopic reagent employed and if exposed to air will quickly convert itself into an aqueous solution. Premelting of the zinc chloride has proved a satisfactory drying technique for this process.

Future Pilot Plant Runs

The present plan is to make two more skull reclamation runs in the pilot plant. The product from several of the final runs will be realloyed in the melt refining runs. If these runs are successful, all future skull reclamation runs will be made in the prototype plant equipment now under development for the Fuel Cycle Facility. The pilot plant would be available, however, for use in pursuing any special problems which might develop as a result of prototype operations.

b. Development of Equipment for Fuel Cycle Facility

Equipment for processing skull oxides in the Fuel Cycle Facility is being built and tested. The basic components of the system consist of a skull reclamation furnace, a material transfer line, waste receiver equipment, and a retorting furnace for recovery of the uranium product.

Furnace for EBR-II Skull Reclamation Process

The reduction of uranium oxide (skull oxide) to metal and the

separation of uranium from fission products will be carried out in one processing furnace. Tungsten appears to be the only suitable crucible material which will resist the corrosive effects of the molten halide salts and zinc used in the skull reclamation process. A pressed-and-sintered tungsten crucible, 23 3/4-in. inside height and 14-in. ID, has been obtained to process charges of skull oxide containing approximately 5 kg of U_3O_8 .

Figure I-9

SKULL RECLAMATION FURNACE (CLOSED)

The furnace body is surrounded by a vertically split 20-kw resistance heater. Each heater half is supported on a steel frame which is hinged to the support column for the furnace cover. Gas-operated, double-action cylinders hold the heaters around the furnace body during the heating cycles and open the heaters during the cooling cycles.

The three ports in the cover are for introduction of the agitator assembly, the transfer line and the charging chute. Around each port and the furnace cover is a fusible metal seal trough and resistance heaters for melting the seal. (The scale of the ruler is in inches.)

The operations to be conducted in the furnace require several heating and cooling cycles. To overcome the effects of fission product heating and to reduce the time necessary for cooling the crucible, a furnace is required which will enhance the rate of heat dissipation. After consideration of various designs, a furnace has been built based upon a Hastalloy C* cylindrical body which fits closely around the tungsten crucible. The furnace body is heated by a 20-kw resistance heater in the form of a hollow vertical cylinder, split

Figure I-10

SKULL RECLAMATION FURNACE (OPEN)

The two heater halves are shown in the open position, which permits the furnace body to cool. Each heater half is rated at 10 kw and is divided horizontally into three independent heater sections to permit close control of the furnace wall temperature.

The furnace body is made of Hastelloy C. The insulated furnace cover is joined to the body by a large fusible metal seal and is supported on the two square steel columns.

-
- * Product of Haynes Stellite Company. The composition is as follows:
 54 w/o nickel, 17 w/o molybdenum, 15 w/o chromium, 5 w/o iron, and 4 w/o tungsten.

axially. The heater halves are externally insulated and are held closed around the body during heating cycles. When the furnace is to be cooled, the heater halves are opened by gas-operated, double-action cylinders to expose the furnace body. Figure I-9 shows the furnace with the heaters in the closed position; Figure I-10 shows the heaters in the open position.

The figures also show the insulated furnace cover, which is joined to the body with a large fusible seal. The three ports visible in the top are for introduction of the transfer line, the agitator assembly, and the charging chute. These components are shown in sectional view in Figure I-11. In Figure I-6, the furnace is shown with the transfer line and the agitator assembly installed.

Figure I-11

SKULL RECLAMATION FURNACE (VERTICAL SECTIONS)

The drawing at the left shows the large tungsten crucible inside the furnace body. The heater sections surround the furnace body and are hinged to the support columns. The insulated cover is shown with the Mo-30 w/o W agitator and the heated Mo-30 w/o W transfer line in position. The drawing at right shows the charging chute, which protects the agitator and transfer line from damage by materials charged to the furnace. The charging chute consists of four Mo-30 w/o W rods, one of which is hollow and serves as a thermocouple protection tube. Skull oxide will be contained in a zinc can when it is charged into the charging chute.

Prior to installation in the furnace, the molybdenum-30 w/o tungsten agitator and shaft seal assembly were tested. With a four-bladed impeller (4-in. dia., 1 1/2 in. high) rotating to discharge downward, vigorous mixing of molten lead or molten zinc was achieved at speeds of about 700 rpm. The shaft seal consists of a lower sleeve bearing made of TS-574 graphite, * an upper ball bearing, and high temperature packing rings between the two bearings. The shaft seal assembly remained essentially leak-tight during the mixing tests. In other tests in which the seal assembly was exposed to a crucible heated to 800°C, no excessive temperatures developed in the assembly.

Figure I-12

SKULL RECLAMATION FURNACE TRANSFER LINE

The line is made of 3/4-in. OD molybdenum-tungsten rod which is gun-drilled to 1/2-in. ID. The longer end of the line dips into the furnace crucible, as shown in Fig. I-11. The rest of the line is wound with 1/8-in. OD resistance heaters which can maintain a temperature of about 800°C to prevent solidification of molten metal or flux during transfer. The heaters are insulated with swaged magnesia and encased in Inconel. The wound section is insulated with Fiberfrax and potassium titanate powder and enclosed in a stainless steel jacket. The bellows assembly located at the discharge end of the transfer line allows for thermal expansion when the transfer line is connected between the furnace and the transfer receiver equipment (see Figure I-13). (The scale of the ruler is in inches.)

The charging chute is made of four molybdenum-30 w/o tungsten rods. Its primary function is to protect the agitator and transfer line from damage during charging of the skull oxide in its zinc storage can (see ANL-6875, p. 72). One rod is drilled to within one inch of the bottom and serves as a protection tube for a thermocouple used to measure temperatures of the crucible contents. Zinc, magnesium, and flux will be charged in granular form.

Transfer Line

The heated transfer line (see Figure I-12) to be used for removal of molten metals and flux from the furnace is made of 3/4-in. OD molybdenum-30 w/o tungsten rods which were gun-drilled to 1/2-in. ID. Two lengths were joined by a threaded coupling and then formed into a J-shape by hot bending over a jig. The part of the tube above the furnace crucible is wound with resistance heaters which can maintain a temperature of about 800°C to prevent solidification of molten metal or flux during transfer. The heated section is insulated and enclosed in a stainless steel jacket to protect the insulation, the heaters, and the tube against mechanical damage. Tests of the transfer line with molten

* A proprietary impregnated graphite, product of National Carbon Company.

metal or flux are planned.

Transfer Receiver

The transfer receiver provides for purging the transfer line, collecting and weighing the transferred material, and collecting furnace fumes which accompany the material. The various components are shown in Figure I-13.

Figure I-13

The materials transferred from the skull reclamation furnace fall into two classes: molten metal wastes and molten flux wastes, which are collected in 22-gauge, 8-gal steel pails, and uranium-zinc-magnesium product solution which is cast into a mold. The receiving container is held in the heavy steel secondary container which rests upon the movable platform scale. When the transfer line is to be purged, the scale is rolled into position under the hood, and the elevating mechanism engages the steel secondary container and lifts it to the top of the hood. At this position a seal is made around the discharge end of the transfer line. An argon pressure line connected to the top of the hood supplies argon for purging the heated transfer line back to the furnace. When material is to be transferred, the secondary container is lowered until it rests on the platform scale. The furnace is then pressurized to about 15 psig to effect the transfer. To control the fumes generated in transfer, a hood and an exhauster system have been provided.

A centrifugal blower draws the process cell atmosphere through the hood and then through a large filter before returning it to the cell.

In experimental tests of the transfer line, molten zinc was successfully transferred into a 22-gauge steel pail. Although molten zinc is corrosive to steel, no evidence of dissolution of the steel pail was noted.

Magnesium-Zinc Retorting Equipment

The final material (Fig. I-7) transferred from the skull reclamation furnace consists of about 4 kg of uranium dissolved in approximately 36 kg (8 liters) of Zn-12 w/o Mg. Plant-scale equipment is under development to recover the uranium by distilling off the volatile magnesium-zinc.

The initial design of the distillation apparatus (see Figure I-14) was selected to fit the base of one of the melt refining furnaces now installed in the Argon Cell of the Fuel Cycle Facility. A compatible design would permit a saving in space and equipment.

A preliminary test of the apparatus indicated that the evaporator, condenser, and collector will function satisfactorily. However, the uncooled copper induction coil, made of 5/8-in. dia. bar stock, overheated at the power level required to maintain an evaporation rate of 100 g/min.* To alleviate this condition, a new induction coil made of 3/8 in. by 2 in. bar stock has been installed to increase the heat radiation surface. Consideration is also being given to a furnace design which utilizes resistance heating.

All the skull reclamation process equipment items described in this report section will be installed in the inert-atmosphere enclosure (see an earlier section of this report) for further testing. Full-scale (5 kg U_3O_8) runs with unirradiated fuel are planned. Installation will be made in the Fuel Cycle Facility as soon as operability and reliability have been demonstrated.

3. Blanket Process

Blanket material discharged from the EBR-II reactor is to be processed to concentrate plutonium from its initial concentration of about 1 w/o to a value of at least 40 w/o in uranium. The blanket process presented in ANL-6875, p. 24, is to be demonstrated on an engineering scale in the pilot plant (Fig. I-6, p. 26, ANL-6766) now used for the skull reclamation process. The blanket process, however, requires the evaporation of more solvent for product recovery than does the skull reclamation process and will require a new distillation unit. Based on the distillation experiments discussed in ANL-6875, pp. 23-25, a new still is being designed and will be installed in the pilot

* This evaporation rate was selected to permit evaporation of a full 36-kg charge in an eight-hour day.

Figure I-14

MAGNESIUM-ZINC DISTILLATION APPARATUS.
36-KILOGRAM SCALE

The product of the skull reclamation furnace, consisting of about 4 kg of uranium and 36 kg (8 liters) of Zn-12 w/o Mg, is charged to the crucible. The charge is heated inductively, and the Zn-Mg vapors rise through the center tube to the condenser. The condensed liquid drains into the graphite distillate collector. The graphite felt and Fiberfrax insulators prevent loss of vapor during distillation and permit the collector to be separated from the secondary-container cover when the apparatus has cooled.

plant glovebox.

4. Purification of Argon from Nitrogen with Titanium Sponge

A method is under development for removing nitrogen from argon by gettering the nitrogen on hot titanium sponge. Although this method has general utility for purifying argon for such applications as glovebox atmospheres, the major incentive for its development is a possible future need to remove nitrogen from the atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility. The nitrogen concentration of the Argon Cell atmosphere averaged about 6 v/o during 1964. Two sets of experimental equipment were constructed for the nitrogen-removal study: (1) equipment for determining the kinetics of nitrogen removal from argon on hot titanium sponge and (2) a pilot plant for obtaining overall process performance data and information on component reliability. Studies are being conducted with argon containing nitrogen concentrations between 100 and 50,000 ppm.

a. Kinetics of Nitrogen Removal from Argon with Titanium Sponge

A gas-circulating loop was built for a study of the kinetics of nitridation of titanium sponge by argon-nitrogen mixtures. In this loop an argon-nitrogen mixture of carefully controlled composition is continuously circulated by a diaphragm pump through a vertical series of eight small test beds, each containing 0.7 to 2 g of titanium sponge. The circulation rate (100 to 800 liters/hr) is such that only a small fraction (less than 5%) of the nitrogen reacts with the titanium sponge in a single pass through the series of beds. By this technique, all beds in the stack are exposed to approximately the same nitrogen concentration in the reacting gas and no correction is required for decreasing nitrogen concentration as the gas moves from bed to bed. The extent of reaction of the titanium sponge metal is determined at time intervals by successively and permanently removing the topmost titanium bed and analyzing it by a modified Kjeldahl analysis for the amount of nitrogen reacted.

Data have now been obtained at nitrogen concentrations of approximately 100, 300, 1000, 5000, and 50,000 ppm in argon. Preliminary reaction rate curves at a temperature of 900°C are presented in Figure I-15. Each curve represents at least two duplicate runs. The rate of reaction becomes very low somewhat after a conversion equivalent to 40% of the titanium to the mononitride. The nature of the reaction products has not yet been established. The asymptotic conversion level appears to be dependent upon the nitrogen partial pressure in the reacting gas.

The apparently lower saturation level of the titanium sponge when reacting with 50,000 ppm nitrogen than when reacting with 5,000 ppm nitrogen is being investigated. It is doubtful that this is a real effect; the anomaly may be caused by scatter of the data at high conversion levels. The scatter in the

Figure I-15

RATE OF REACTION OF NITROGEN IN ARGON WITH TITANIUM SPONGE

Temperature: 900°C
Assumed Reaction: $2\text{Ti} + \text{N}_2 \rightarrow 2\text{TiN}$

data between duplicate runs is generally about 10% of the conversion level, and scatter of this magnitude could account for the apparent crossing of the curves.

Experiments to determine the saturation level of the titanium sponge are now in progress. Efforts are also being made to determine the effective surface area of the titanium sponge and the phases present in the reacted sponge. The effect of temperature on the reaction will also be cursorily examined.

The mechanism of the reaction has not been determined, but the rate-controlling step is probably diffusion of nitrogen in the solid phase, as evidenced by the fact that the reaction rate is relatively insensitive to variations in the gas flow rate (checked at superficial linear velocities ranging from 0.3 to 1.0 ft/sec). In addition, metallographic examination of

reacted sponge particles indicates the presence of a surface film which appears to grow as the reaction proceeds. The increasing resistance of this boundary layer to the diffusion of nitrogen would gradually slow down the reaction, resulting in reaction rate curves like those shown in Figure I-15. Interpretation of the data is now in progress. An attempt will be made to correlate all the data into a single equation which will be useful for the design of engineering-scale equipment.

b. Pilot Plant for Nitrogen Removal from Argon

A pilot plant unit, designed to demonstrate the removal of nitrogen impurity from argon gas on a large scale, operated for about 1800 hr during 1964. This unit, which operated at a gas circulation rate of 10 cfm and nitrogen concentrations of 100 and 650 ppm in argon, provided information on component design and reliability for large-volume purification systems. The system is pictorially presented in Figure I-16. Detailed information on the design and flow pattern of this system is presented in ANL-6875, p. 14.

Figure I-16

PILOT PLANT FOR STUDY OF NITROGEN REMOVAL FROM ARGON

Continuous operation of the loop began on March 13, 1964, and continued until 1000 hr of operation had been accumulated. At that time the unit was shut down for inspection and recharging of the titanium sponge bed. During the initial period of operation of the loop, all components and instrumentation performed their design functions well. In this initial period of operation the performance of the titanium sponge bed was difficult to assess because the loop had been exposed to air and water vapor during startup operations. Even so, efficient removal of nitrogen from argon gas containing 650 ppm nitrogen was realized for a period of about 150 hr. Analysis of the titanium sponge removed after 1000 hr of operation (150 hr with nitrogen in the gas) showed an average conversion equivalent to 42.2% of the titanium to the mononitride. This average conversion is encouraging since it is about the maximum conversion obtained in kinetic studies (see Fig. I-15) and represents a cost of titanium gettering material of about \$11 per pound of nitrogen removed. A similar calcium gettering system would cost at least \$15 to \$20 per pound of nitrogen removed if conversion of 40 to 60% of the calcium to Ca_3N_2 were attained. Other factors such as the operating temperature, pyrophoricity, and materials of construction also affect overall economics, but at the present time it appears that titanium-gettering is the most economical process.

Inspection of the loop after 1000 hr of operation disclosed no evidence of deterioration of any process vessel. The loop was restarted at a gas concentration of 100 ppm nitrogen in argon. Shutdown of the loop was required after 650 hr of continuous operation because the failure of two blower shaft seals permitted oil to leak into the interior of the blower and subsequently into the circulating gas. During this 650 hr of loop operation, the titanium sponge bed lowered the nitrogen concentration in the circulating gas to less than 20 ppm, the lower limit of detection. Analysis of the titanium sponge indicated an average conversion of about 30% (representing a gettering cost of \$15 per pound of nitrogen removed). The conversion might have been higher had the oil not contaminated the system, including the titanium bed, and forced a premature shutdown of the loop.

The blower was repaired by replacing the seals that had failed and increasing the seal lubrication, but seal failure again occurred after an additional 150 hr of operation.

The pilot plant loop has achieved its design purposes by successfully demonstrating removal of nitrogen impurity from argon gas on a large scale with favorable economics. All components and instrumentation except the blower were adequate for plant-scale equipment. It is believed that the gas-circulation problem could be solved by substituting a multistage centrifugal compressor similar to those used in the EBR-II Argon Cell.

c. Corrosion of Nickel, Molybdenum, and Tungsten Alloys by Argon-5% Nitrogen

The possible detrimental effect of the argon-5% nitrogen atmosphere present in the Argon Cell of the EBR-II Fuel Cycle Facility on alloys which may see service in the Facility is being investigated. Brunhouse¹ of Aerojet General Nucleonics reports that Inconel 600 and Hastelloy X alloys react with high-purity nitrogen at temperatures above about 650°C, causing serious embrittlement of the alloys. The reaction appears to result in the formation of a complex nitride phase and is probably common to most nickel-rich alloys. The effect appears to be enhanced in alloys which also contain molybdenum. Since the reaction is not noticed when these alloys are exposed to air, it is believed that oxygen inhibits the reaction.

The use of nickel-rich alloys in the Argon Cell is required, since these alloys are about the only easily available materials with sufficient structural strength to permit use in applications which require temperatures of 900°C. A specific application of these alloys is for the construction of the skull reclamation furnace, the exterior surfaces of which are expected to reach 900°C at times during an operating cycle.* Consequently, a program has been initiated to study the possible detrimental effect of argon-5% nitrogen on various materials which may see service in the Argon Cell. These alloys include tungsten and molybdenum-30% tungsten, as well as the nickel-bearing alloys, Inconel 600, Inconel 800, Hastelloy C, Hastelloy X, and types 304 and 316 stainless steel.

Exposure tests of these alloys for 1000 hr at 900°C have been completed (see results in Table I-1). After 1000 hr exposure, Hastelloy C, Hastelloy X, and Inconel 800 coupons (2 in. by 1/2 in. by 0.060 in. thick) had become embrittled to the extent that they could not be bent 180° on a radius equal to approximately twice the specimen thickness without cracking. They were not so brittle, however, that reasonable physical shock would cause cracking. Inconel 600 still possessed some ductility and passed the bend test. Metallographic examination revealed the existence of the complex nitride phase in both Hastelloy and both Inconel alloys. This phase extended from the surface exposed to nitrogen, along the grain boundaries, and into the matrix, probably causing embrittlement of the alloys. Tungsten, molybdenum-30% tungsten alloy, and types 304 and 316 stainless steel were affected very little except

¹ Brunhouse, J. S., Corrosion and Compatability of Nickel-based Alloys with High Purity Nitrogen, paper presented at the 13th Annual AEC Corrosion Symposium, Argonne, Illinois, May 1964.

* Under steady state conditions of fuel flow, it should be necessary to operate the skull reclamation furnace about twice a month. Under unusual conditions, operation should be no more frequent than about once a week. Each run will last about 18 hr and the furnace will be above 650°C for about 12 hr and at 900°C for about 4 hr.

Table I-1

EXPOSURE OF METAL COUPONS TO ARGON-5% NITROGEN ATMOSPHERE

Temperature: 900°C
Exposure Time: 1000 hr

<u>Material</u>	<u>Weight Change (mg/cm²)</u>	<u>"2T" Bend Possible^a</u>
Inconel 600	0.68	Yes
Inconel 800	3.14	No
Hastelloy C	2.10	No
Hastelloy X	1.87	No
304 SS	0.73	Yes
316 SS	2.60	Yes
MO-30 w/o W	0.16	-
W	0.33	-

^a After exposure each coupon is bent 180° on a radius equal to approximately two times ("2T") the specimen thickness. All coupons except the tungsten and Mo-30 w/o W would pass the "2T" bend test prior to exposure.

for the formation of slight nitride surface layers.

It is doubtful that nitridation will present a serious problem in the EBR-II cell because high-nickel alloys will be at temperatures above 650°C for limited periods. It is possible, however, that the nitridation effect will limit the useful lifetime of these alloys in the cell atmosphere. Should this problem develop, protection methods such as oxide scaling or diffusion-bonded coatings of these alloys will be used.

B. Processes for Fast Breeder Reactor Fuels

Advanced pyrochemical processes are being developed for the recovery of plutonium and uranium from future EBR-II fuels and from fast breeder reactor fuels in general. Although the initial development effort has been focused mainly on metallic fuels, the processes currently under investigation are also adaptable to ceramic fuels such as carbides, oxides, and possibly nitrides, sulfides, and phosphides. Metallic core fuels are expected to consist primarily of uranium alloyed with about 10 to 20 w/o plutonium, and stabilizing additives such as fissium, titanium, or zirconium. Blanket elements will probably consist of unalloyed natural or depleted uranium. At the present time, refractory metal alloys, e. g. an alloy of titanium and vanadium, are receiving serious consideration as cladding materials for both core and blanket elements. Because the development of high-performance fuels for fast breeder reactors is

still in an early stage, the emphasis in fuel reprocessing studies has been placed on basic separations that can be used in a variety of process flow-sheets.

The objectives of the advanced processes are to remove the bulk of the fission products, to extract bred plutonium from the blanket, to re-enrich the core with plutonium, and to repair radiation damage. To achieve these objectives, separations of cladding material, uranium, plutonium, and fission products from one another are required. Remote operation of all steps will probably be a necessity, even if complete fission product removal were achieved, because of the buildup of radioactive isotopes of uranium and plutonium during long irradiations.

1. General Process Development

To provide a guide for development work, the following reference fuel has been selected:

	<u>Core</u>	<u>Blanket</u>
Type of Alloy	U-Pu-Fs ^a	U
Batch Size	152 kg	371 kg
Cladding	30 kg V-20 w/o Ti	56 kg V-20 w/o Ti
Irradiation	4 a/o burnup	0.1 a/o burnup

Composition after Irradiation

Uranium	112 kg	363 kg
Plutonium	25.7 kg	7.4 kg
Fissium	6.1 kg	none
Fission Products	8.0 kg	0.6 kg

The above specifications are derived from the Argonne Reference Metal Fuel Fast Breeder Reactor, a conceptual 1000 Mw(e) reactor which is the subject of economic study of fuel cycles. The batch size is based on a processing rate of two batches per week.

Several alternative separation steps that might be combined in various ways to make up a process for this type of fuel are listed in Table I-2. Although different combinations of these steps together with the possibility of choosing different solvents and reagents could, in theory, lead to a large

^a Fissium is a collective term signifying the use of a number of fission product elements as alloying elements in the fuel. In this fuel, concentrations of fission product alloying elements are: 2.5 w/o molybdenum, 2 w/o ruthenium, 0.26 w/o rhodium, 0.19 w/o palladium, 0.1 w/o zirconium, and 0.01 w/o niobium.

number of specific process flowsheets, the practical combinations are severely limited by the incompatibility of certain steps with each other and by factors such as waste volumes, reagent costs, and corrosion problems.

Table I-2

ALTERNATIVE SEPARATION STEPS FOR REFERENCE METAL FUEL FOR CONCEPTUAL ARGONNE FAST BREEDER REACTOR

Separation of Fuel from Cladding

1. Disintegration of fuel element by hydriding-dehydriding, followed by:
 - a. selective dissolution of fuel in molten salt and cladding in liquid metal,
 - b. selective dissolution of fuel in liquid metal, or
 - c. physical separation of fuel from cladding fragments.
2. Complete dissolution of fuel and cladding in liquid metal and subsequent chemical separations.
3. Complete dissolution of fuel and cladding in molten salt and subsequent chemical separations.
4. Chlorination in molten salt to volatilize titanium-vanadium cladding as TiCl_4 and VCl_4 .
5. Mechanical decladding.

Separation of Noble Metal Fission Products from Fuel

1. Selective chlorination of uranium and plutonium, and extraction into molten salt.
2. Selective reduction of noble metals and extraction into liquid cadmium, zinc, or copper.
3. Extraction of noble metals into alkali or alkaline earth metal solvents.

Separation of Refractory Metals (Zr, Nb, Ti, V) from Fuel

1. Selective reduction from molten salt solutions by liquid metals.
2. Chlorination, followed by distillation of volatile chlorides.
3. Separations based on solubility differences in liquid metal solutions.
4. Collection of refractory metals on scavenging agents such as tantalum or graphite.

Separation of Rare Earths and Group I and II Fission Product Elements From Fuel

1. Selective extraction of fission products from liquid metal solution into molten salt.
2. Selective extraction of uranium and plutonium from molten salt solution into liquid metal solvent.

(Cont.)

Table I-2 (Cont'd)

3. Extraction of fission products from molten fuel into molten salt (halide slagging).
4. Separations based on solubility differences in liquid metal solutions.

Separation of Plutonium from Uranium

1. Selective extraction of plutonium from liquid metal solution into molten salt.
2. Extraction of plutonium from molten fuel into molten salt (halide slagging).
3. Separations based on solubility differences in liquid metal solutions.

Uranium-Plutonium Recovery from Liquid Metal Solutions

1. Vacuum distillation (retorting) of solvent metals.
2. Electrowinning or electrorefining.

Salt Purification

1. Reduction of rare earths and consolidation into metal ingots.
2. Removal of Group I and II fission product elements by ion exchange.

A conceptual flowsheet for processing the reference core fuel is outlined in Figure I-17. In this scheme, a hydriding-dehydriding treatment is used to disintegrate the fuel and cladding; then the cladding fragments are separated physically by flotation in liquid cadmium. Uranium and plutonium are removed from the cadmium solution by oxidation with CdCl_2 and extraction into molten NaCl-KCl-MgCl_2 . The noble metal fission products (fissium elements) remain in the cadmium solution. Fission product zirconium and niobium are then removed from the molten salt solution by controlled reduction with a small amount of cadmium-magnesium alloy and extraction into that alloy. The uranium and plutonium are then reduced with Na-K-Mg-Cd alloy and are recovered as the metals by vacuum distillation (retorting) of the cadmium and magnesium. The rare earth fission products remain in the salt solution. A sufficient amount of the cadmium-noble metal solution is added prior to retorting to reconstitute the fissium alloy. Waste salt from the process is treated with a small volume of aluminum-magnesium alloy, which reduces and consolidates the rare earths in an ingot, and the bulk of the purified salt is recycled to the process. The same flowsheet is adaptable to the reference blanket material by making two modifications: a plutonium-uranium separation step is inserted after the rare earth separation step, and none of the cadmium-noble metal solution is added to the retorting step.

Figure I-17

CONCEPTUAL FLOWSHEET FOR PROCESSING URANIUM-PLUTONIUM ALLOY FUEL

2. Separation of Fuel from Cladding

Although mechanical decladding is used for the present EBR-II fuel, this method may not be feasible for future high-performance fuels because extensive irradiation is likely to cause metallurgical bonding between the fuel and cladding. Therefore, various chemical methods for separating the fuel and cladding are being investigated. For vanadium-20 w/o titanium cladding, two approaches have been under study -- chlorination and hydriding.

Exposure of uranium fuel pins clad with vanadium-20 w/o titanium to chlorine gas in a molten chloride bath at 600 to 700°C resulted in the formation of soluble UCl_4 and volatilization of the vanadium and titanium as the tetrachlorides. Typical experimental results are shown in Table I-3. By using the proper proportions of alkali and alkaline earth chlorides, it is possible to adjust the complexing power of the melt so that vanadium and titanium chlorides are volatilized without incurring significant uranium losses by volatilization. When a uranium-fission alloy was chlorinated by this method, the reaction rate was slower than for uranium, and an undesirable volatilization of

Table I-3

CHLORINATION OF URANIUM AND VANADIUM-20 w/o TITANIUM
CLADDING IN MOLTEN CHLORIDE MEDIA

Temperature: 600-700°C

Salt Composition	Time (hr)	Material Volatilized (%)	
		U	V, Ti
50 m/o NaCl-32 m/o CaCl ₂ -18 m/o BaCl ₂	1.3	2.7	99.9
50 m/o KCl-32 m/o CaCl ₂ -18 m/o BaCl ₂	1.5	0.9	99.8
40 m/o NaCl-30 m/o KCl-30 m/o CaCl ₂	0.7	0.5	99.8
33 m/o NaCl-40 m/o KCl-27 m/o CaCl ₂	0.8	<0.1	99.8
50 m/o NaCl-50 m/o KCl	0.7	0.1	94.5

most of the molybdenum and zirconium in the fission occurred.* Although the chlorination studies indicated that a separation of uranium from vanadium-20 w/o titanium is chemically feasible, the procedure has serious practical disadvantages such as corrosion, the production of large amounts of liquid chlorides, and partial loss of fission elements.

The hydriding technique is believed to be more promising than chlorination. When uranium-fission alloy or uranium-plutonium-fission alloy clad with vanadium-20 w/o titanium was exposed to hydrogen at about 2 atm pressure and about 250-300°C, the hydrogen apparently diffused through the cladding and reacted with the fuel. The resulting volume increase caused the fuel to become powdered and the cladding to split into fragments. This treatment, followed by a dehydriding step, may permit dissolution of the fuel in a liquid metal or molten salt in which the cladding alloy is insoluble. If the fuel is dissolved in a high-density liquid metal such as cadmium, separation of the relatively light cladding fragments by flotation may be possible.

3. Distribution of Fuel Constituents Between Liquid Metals and Molten Salts

Many of the separations in the processes currently under investigation are effected through differences in the distribution behavior of the fuel

* During the course of this work an interesting side-result was obtained in that immiscible liquid phases were observed at certain composition regions in the quaternary salt systems NaCl-KCl-CaCl₂-UCl₄ and KCl-CaCl₂-BaCl₂-UCl₄. In the latter system, chemical analyses showed the lower phase to contain mostly KCl and UCl₄, whereas the upper phase consisted mainly of CaCl₂ and BaCl₂.

constituents between liquid metals and molten salts. Measurements of pertinent distribution coefficients* have therefore been continued. In all cases, the molten salt phase was the ternary system, 30 m/o NaCl-20 m/o KCl-50 m/o MgCl.

One of the primary separations involves the use of a molten salt to extract rare earths and other electropositive fission products from uranium and plutonium in a liquid metal solution. Experiments were performed to determine the distribution coefficients of praseodymium, a representative rare earth, between the salt and cadmium-magnesium-zinc alloys as a function of alloy composition. The results at 600°C are presented in Figure I-18. For an adequate separation of praseodymium from uranium and plutonium, the praseodymium distribution coefficient should have a value greater than unity. This condition exists in the magnesium-rich and cadmium-rich regions of the diagram.

Figure I-18

DISTRIBUTION COEFFICIENT $\left(\frac{\text{w/o Pr in salt}}{\text{w/o Pr in metal}} \right)$ OF PRASEODYMIUM
BETWEEN 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂ AND CADMIUM-
MAGNESIUM-ZINC SYSTEM AT 600°C

* Distribution coefficient, $K_d = \frac{\text{w/o element in salt phase}}{\text{w/o element in metal phase}}$

in Figure I-18. (Partial data were presented previously in ANL-6875, Figure I-9, p. 29.) At very low magnesium concentrations, the system is too unstable for reliable process operation because of the very strong dependence of the distribution coefficients upon the magnesium concentration. A typical liquid metal solvent composition that has been selected for some process flowsheets is 70 a/o cadmium-15 a/o magnesium-15 a/o zinc. Under these conditions, pertinent separation factors (S.F.) at 600°C are as follows:

Elements		S.F. = $K_d(A)/K_d(B)$
A	B	
Pr	Pu	43
Pr	U	51
Pu	U	1.2

Figure I-19

DISTRIBUTION OF PRASEODYMIUM BETWEEN 30 m/o NaCl-20 m/o KCl-50 m/o $MgCl_2$ AND BINARY MAGNESIUM ALLOYS AT 600°C

The distribution coefficients and separation factors for this system are such that about six stages would be required for an adequate separation of praseodymium (and consequently other rare earth fission products) from uranium and plutonium. The uranium-plutonium separation factor is too small for a practical separation of these two elements. However, such a separation is possible by increasing the magnesium content of the liquid metal to precipitate the uranium. The supernatant liquid metal, which contains all of the plutonium in solution, is contacted with the salt to extract the plutonium. Practically no uranium is extracted because of its very low solubility under these conditions. The salt and metal phases are then separated.

To reduce the cost of storing radioactive salt wastes, treatment of the effluent salt from the rare earth extraction step with a liquid metal to reduce the rare earths and consolidate them in a small metallic ingot is an attractive possibility. The purified salt would be recycled to the process. In this connection, distribution coefficients of praseodymium between the NaCl-KCl- $MgCl_2$ system and various binary alloys of magnesium at 600°C were determined. The

results appear in Figure I-19. Among the systems examined, aluminum-magnesium proved to be the most effective alloy for extracting the praseodymium from the salt, and it also appears to be the most attractive system from a practical viewpoint. Consequently the aluminum-magnesium system was investigated further to determine the distribution coefficients and solubilities of several other rare earths. The results are listed in Table I-4. Each of the elements examined (Y, La, Ce, Pr) exhibited retrograde solubility above about 700°C, which suggests a change in the equilibrium solid

Table I-4

DISTRIBUTION COEFFICIENTS OF RARE EARTH ELEMENTS BETWEEN
ALUMINUM-MAGNESIUM ALLOY AND NaCl-KCl-MgCl₂ AND THEIR
SOLUBILITIES IN THE ALLOY

Liquid Metal Phase: Al-20 w/o Mg (saturated with rare earth)^a

Molten Salt Phase: 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂

Element	Distribution Coefficient, Kd		Solubility in Metal Phase (w/o)	
	550°C	600°C	550°C	600°C
Y	2.42×10^{-3}	4.39×10^{-3}	0.91	3.45
La	2.83×10^{-3}	7.03×10^{-3}	2.23	4.65
Ce	4.12×10^{-4}	7.08×10^{-4}	2.24	3.27
Pr	----	4.4×10^{-4a}	2.53	3.91

^aThe distribution coefficient for praseodymium is from previous data in which the metal phase was not saturated (i.e., at a Pr concentration of 1.6 w/o).

phase at this temperature. The distribution and solubility data indicate that recycled salt can be processed effectively in a single-stage contact with aluminum-magnesium alloy to form a highly concentrated metallic waste. Aluminum contamination of the salt (2.3×10^{-3} w/o) was sufficiently low to avoid significant contamination of the uranium and plutonium products from the process. If desired, the waste ingot could be alloyed with other materials, such as copper, to form a higher melting, more corrosion-resistant material.

The high praseodymium distribution coefficient shown for copper-magnesium alloy in Figure I-19 suggests the possibility of using this alloy as a liquid metal phase for the separation of rare earth fission products from uranium and plutonium. Simultaneous measurements of the distribution coefficients of praseodymium, uranium, and plutonium between the NaCl-KCl-MgCl₂ system and copper-magnesium alloys yielded the data in Figure I-20.

Pertinent separation factors from these data are as follows:

Elements		S.F. = $K_d(A)/K_d(B)$	
		600°C	800°C
A	B	Cu-39.5 w/o Mg	Cu-20 w/o Mg
Pr	Pu	162	167
Pr	U	1500	5660
Pu	U	9	34

Figure I-20

CODISTRIBUTION OF PRASEODYMIUM, PLUTONIUM AND URANIUM BETWEEN 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂ SYSTEM AND COPPER-MAGNESIUM ALLOY

In this system the separation factors are sufficiently large that a single-stage extraction might be adequate for the separation of rare earths from plutonium and uranium. Furthermore, the plutonium-uranium separation factor is much larger than that for the cadmium-zinc-magnesium system. Again, because of the low solubility of uranium (0.005 w/o at 600°C) in the copper-39.5 w/o magnesium alloy, an efficient separation of plutonium by molten salt extraction should be feasible. The disadvantage of the copper-magnesium system is that the liquid metal solvent cannot be removed by distillation, so additional oxidation-reduction steps are needed to recover the products. The choice between copper-magnesium and cadmium-zinc-magnesium as a process solvent depends in large measure upon the head-end and product recovery steps and other factors, including corrosion, operating temperatures, and multi-stage vs single-stage extraction equipment.

4. Solubility of Uranium and Plutonium in Cadmium-Zinc-Magnesium Alloys

The ternary system, cadmium-zinc-magnesium appears attractive as a process solvent because lower operating temperatures are possible and it is less corrosive than magnesium-zinc alloys toward stainless steel equipment. The effect of solvent composition on uranium and plutonium solubilities

is of importance in minimizing the volumes of process solutions. A contour plot showing the solubility of uranium in cadmium-zinc-magnesium alloys at 600°C as a function of solvent composition was presented earlier (ANL-6875, Figure I-7, p. 27). These data, along with other considerations (low melting point, acceptable corrosion rates in type 405 stainless steel, distribution coefficients that permit selective extraction of rare earth fission products into molten NaCl-KCl-MgCl_2), led to the conclusion that the cadmium-rich region of this system offers the optimum process conditions. Subsequent determination of the solubility of plutonium in this region produced the data shown in Figure I-21. In general, the solubility of plutonium is a factor of three to six higher than that of uranium in this composition region. Since uranium-plutonium fuels will contain much less plutonium than uranium, the uranium solubility will limit the amount of fuel in the solution. Cosolubility measurements showed that a small amount of plutonium is carried with uranium precipitated from the solution. By way of comparison, extensive coprecipitation of plutonium

Figure I-21

SOLUBILITY OF PLUTONIUM IN CADMIUM-ZINC-MAGNESIUM ALLOYS

with uranium occurs in zinc solution (ANL-5789, p. 89), whereas it is negligible in liquid magnesium.

5. Solution Stability Tests

Uranium and plutonium in metal solutions are susceptible under certain conditions of temperature and solution composition, to precipitation by reaction with the container elements or solution impurities such as corrosion products. To evaluate several potential container materials, solutions of plutonium in 70 a/o cadmium-15 a/o zinc-15 a/o magnesium together with a salt composed of 30 m/o NaCl-20 m/o KCl-50 m/o $MgCl_2$ were held in 1020 mild steel, type 304 stainless steel, and type 405 stainless steel for 100 hr at 600°C. Both the metal and salt phases were sampled periodically for plutonium analysis. The plutonium material balances were 65% for 1020 steel, 96.8% for type 304 stainless steel, and 98.7% for type 405 stainless steel. The data indicate that 1020 steel is probably unsatisfactory. The 98.7% plutonium material balance for type 405 stainless steel indicates that little, if any, loss of plutonium occurred under these conditions. These results support the belief that the 400 series stainless steels show the greatest promise for use in process vessels. Work is also in progress on the stability of uranium solutions.

6. Processes for Oxide and Carbide Fuels

Cursory cost estimates have indicated that the advanced pyrochemical processes should compete favorably with other processes for ceramic fuels, particularly for carbides. A considerable effort involving laboratory and pilot plant demonstrations of selected flow sheets for processing ceramic fuels has been planned.

7. Halide Slagging of Uranium-Plutonium Alloys

A preliminary study has been completed on the feasibility of selectively extracting highly electropositive fission product elements, such as the rare earth, alkali, and alkaline earth elements, from molten uranium-plutonium-fissium alloys into an overlying molten halide salt layer or flux. The process, which is of the melt refining type, is called "halide slagging". The attractive features of this process are a short operating time (about 1 hr at temperature), relatively low operating temperature ($\sim 1150^\circ\text{C}$), and a high product yield ($>96\%$).

In runs with metal charges of about 700 g, the molten phases were satisfactorily contained in isopressed, high-density beryllia crucibles. These crucibles are resistant to attack by the metal and flux phases, and permeation of the walls by molten flux (75 m/o $BaCl_2$ -25 m/o $CaCl_2$) appears to be low. Flux and metal phases were separated by cooling the system to about 860°C to solidify the metal phase, and then by pouring off the still-molten salt layer. The metal phase was subsequently remelted and poured into a different mold

Table I-5

MELT REFINING OF PLUTONIUM-CONTAINING FUELS BY USE OF HALIDE FLUXES

All runs liquated at 1150°C for 1 hr under argon, flux poured off at 860°C, and ingot poured at 1300°C.

Metal Charge Composition (w/o): 80.97 U, 10.02 Pu, 9.01 fission plus cerium as listed.

Fission Composition (w/o): 2.87 Mo, 3.20 Ru, 0.54 Rh, 1.13 Pd, 0.93 Zr

Flux Composition (m/o): 75 BaCl₂, 25 CaCl₂

Crucible: Isopressed, high-density, high-purity BeO

Run No.	Metal Charge		Oxidant		Ingot Yield (%)	Ce Removal from Ingot (%)	Pu Transferred to Flux (% of Pu in charge)	Ce/Pu Separation Factor ^a
	Wt. (g)	Ce (w/o)	Material	Percent Theoretical				
HVC-5	737	0.335	No oxidant added		97.1	62.3	0.05	--
HVC-17 ^b	696	0.721	MgCl ₂	81	93.6	93.1	0.09	2300
HVC-7	743	0.335	MgCl ₂	110	98.3	98.2	0.45	7400
HVC-10	716	0.468	MgCl ₂	110	97.5	97.6	0.29	7200
HVC-11	691	0.751	MgCl ₂	200	96.9	99.1	1.88	4100
HVC-14 ^b	652	0.648	MgO	200	96.3	92.6	0.66	900
HVC-18	596	0.694	CaO	200	96.5	92.0	0.004	7100

^a Separation Factor = $\frac{\text{Ce in Flux/Ce in Metal}}{\text{Pu in Flux/Pu in Metal}}$. Ce and Pu values are weight percent at the end of a run.

^b Both flux and metal poured at 1300°C. Separation effected by mechanically breaking solid flux away from metal.

at 1300°C. An alternative procedure is to pour both phases together and subsequently break apart the solidified metal and salt phases. Yields of purified metal have been about 96%. This figure should be higher for plant-scale charges.

Table I-5 shows that nearly complete extractions of cerium (a stand-in for all highly electropositive fission products) from a synthetic spent fuel alloy of molten uranium-10 w/o plutonium-10 w/o fission alloys by molten salts has been realized within 1 hr at 1150°C. In the earlier runs, MgCl₂ in a CaCl₂ - BaCl₂ flux was used to oxidize the cerium and thereby effect its transfer to the molten salt phase. In later runs, both MgO and CaO were used as oxidants. When 110% of the amount of MgCl₂ required to oxidize all of the cerium to CeCl₃ was employed, 98% of the cerium was removed along with less than 0.5% of the plutonium. However, when the amount of MgCl₂ was increased to 200% of that required for complete oxidation of the cerium, the plutonium transferred to the salt phase was increased to about 2%. When CaO was used as the oxidant, the amount of plutonium transferred to the salt phase was substantially reduced (to only 0.004% when a 100% excess of CaO was used), but the cerium-to-plutonium separation factor (see definition in Table I-5) remained at the same high value as that obtained with MgCl₂ (~7000). Thus, the use of this oxidant obviates the necessity for an accurate estimate of burn-up in order to size the oxidant charge. Plutonium vaporization was very low (<0.1%) for all oxidizing agents.

On a laboratory scale, a single experiment was performed to determine the behavior of fission product zirconium in the halide slagging process. A synthetic alloy consisting of uranium, 5 w/o fission, 0.68 w/o zirconium, and 0.45 w/o cerium was contacted with a CaCl₂ - MgCl₂ flux in a high purity beryllia crucible under an argon atmosphere for 1 hr at 1200°C. The MgCl₂ content of the flux was 60% in excess of the stoichiometric requirement for complete oxidation of the cerium and zirconium. The zirconium removal resulting from this treatment was negligible. The cerium removal of 97% was in good agreement with results given in Table I-5.

Small-scale experiments are being made to determine the extent of plutonium removal from uranium-plutonium alloys that can be achieved by halide slagging. Uranium-plutonium alloys containing about 2 to 5 w/o plutonium are melted and held in contact with CaCl₂ - UCl₃ fluxes with varying amounts of UCl₃ for periods of 15 to 90 min and at temperatures in the approximate range of 1175 to 1225°C. The purpose of the experiments is to determine equilibrium constants for the reaction:

If favorable equilibrium constants are found, this procedure may prove useful for the extraction of plutonium from fast breeder reactor blanket material.

8. Development of Engineering Equipment and Procedures for Molten Metal-Salt Extraction Operations

A key operation in the process for advanced plutonium-containing reactor fuels is a countercurrent extraction operation for separation of plutonium and uranium from rare earth elements (see flowsheet in Fig. I-17).

The engineering feasibility of continuous countercurrent extraction, as opposed to batch countercurrent extraction, is being investigated. Continuous processes generally require less space and less direct manipulation than batch processes. These advantages may be especially important in shielded facilities in which space is expensive and any handling of the equipment must be done remotely.

The initial objective of this program is the construction and operation of a countercurrent extraction column in which the two solvent phases will be a cadmium-base metal alloy and a halide salt. Uranium and rare earths will be the distributing solutes. The objectives will be to determine the capability of an extraction column to extract and separate various elements and to demonstrate the performance of components such as valves, pumps, and flowmeters which are required for any flow process.

The current work on this program has been to gather preliminary information on the general feasibility of continuous pyrochemical processing. The initial studies are expected to lead to the construction of a high temperature extraction facility. The present work includes (1) the conceptual design of the high temperature extraction facility, (2) the construction of a facility to test system components, (3) the development of various types of instruments which are suitable for high-temperature service, (4) the estimation of mass transfer rates of uranium and rare earths between liquid metals and salts, (5) the development of a practical method of purifying the chloride salt solvents used in the fuel recovery processes, and (6) the selection of materials of construction which are resistant to attack by the liquid metals and salts of interest.

a. Design of High-Temperature Extraction Facility

A conceptual design has been made of a high temperature extraction facility which will be placed in the resistance furnace previously used for a cadmium distillation unit (see ANL-6800, p. 127). The extraction facility consists of a 1-in. dia., 18-in. long packed column, four tanks to hold the salt and metal feeds for the column and to contain the effluents from the column, constant-head tanks to control feed rates to the column, and centrifugal pumps to circulate the fluids. Valves, flowmeters, liquid level detectors, and column interface controllers are also required. The equipment will be fabricated from type 405 stainless steel, which exhibits good corrosion resistance to the metal-salt system under consideration (see part e of this section).

b. Component Test Loop

A facility has been constructed for the purpose of testing components for eventual use in the high-temperature extraction unit. A drawing of the test loop is shown in Figure I-22. Liquid metal or salt is circulated by a pulse pump from the lower surge tank to the upper tank. The liquid flows by gravity from the upper tank into the lower tank to complete the circuit. The two bottom tanks are used only in filling or draining the system. The facility was designed to allow isothermal operation ($\pm 10^\circ\text{C}$) at selected temperatures between 450 and 650°C , using resistance heaters. The loop has been designed to allow the insertion of various items of equipment to test their performance when used with liquid metal and molten salt systems. Construction of the facility has been completed, and initial shake-down runs have been started.

The first test will involve the circulation of a 50 m/o MgCl_2 - 30 m/o NaCl - 20 m/o KCl salt (m.p. 396°C) to determine the reliability of the heating technique, various types of valves, a flowmeter, and a pulse pump.

Figure I-22

ENGINEERING TEST LOOP FOR MOLTEN METAL AND SALT SYSTEMS

Construction has begun on a 4-ft (1-in. dia.) prototype packed column to be installed in the loop for the contacting of countercurrent streams of metal and salt.

c. Preliminary Extraction Studies

Attempts are being made to measure the rate of transfer of uranium and rare earths between chloride salts and cadmium-base alloys. This information will then be used to predict the performance of countercurrent liquid-liquid extraction columns and to judge the feasibility of using columns to separate actinides from rare earths. Other investigations using similar liquid metal-salt systems have shown that the mass transfer rate is reasonably rapid. Studies have been made at Brookhaven of the transfer of a rare earth solute from single drops of metal into salt² and in countercurrent extraction columns.³ A metal phase of bismuth-magnesium and a salt phase of 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl were used in these studies. The reported results indicate that mass transfer coefficients obtained in aqueous-organic systems and based on the two-film theory⁴ yield reasonable approximations of mass transfer rates in metal-salt systems and support the hypothesis that a packed extraction column is practical for cadmium-base alloy systems. However, it is not possible to predict reliably the performance of a column.

It is expected that good agitation of the metal phase will be required if practical extraction rates are to be achieved. In most process applications envisioned for metal-salt columns, the metal will be the discontinuous phase. In ordinary situations the discontinuous phase would be expected to be less turbulent than the continuous phase. However, in work in this Division, motion pictures of a packed column in which Wood's metal (50 w/o bismuth, 27 w/o lead, 13 w/o tin, and 10 w/o cadmium; melting point, 70°C) was passed countercurrently to water at 90°C have shown that there was a high degree of turbulence in the discontinuous phase as a result of metal droplets falling on pools of metal. The metal tended to collect in pools at specific sites in the packing. When struck by drops, the pools tended to vibrate and break into smaller droplets which then fell to pools below. It would appear that there was a high degree of agitation in the falling drops because of their mode of formation.

To simulate the operation of a countercurrent packed column, a Cd-3 w/o Mg-0.5 w/o U alloy was poured into a static column of molten purified 30 m/o NaCl -20 m/o KCl -50 m/o MgCl_2 which was contained in a 7/8-in. ID quartz tube. Several runs were performed in which the central 6-in. section of the tube was loaded with each of several types of packing. When most of the

² Katz, H. M., Hill, F. B., and Speirs, J. L., Trans. Met. Soc. AIME 218, 770 (October 1960).

³ Hill, F. B., and Kukacka, L. E., Jr., BNL-791, January 1963.

⁴ Handlos, A. E., and Baron, T., AIChE J. 3, 129 (1957).

metal had fallen through the packing and collected in the bottom of the tube, the tube was cooled rapidly to minimize transfer across the metal-salt interface at the tube bottom. The metal was in contact with molten salt for 1 to 5 min. The amount of uranium required to saturate the salt phase at equilibrium was negligible compared with the amount of uranium charged initially. The limiting extraction attainable in these transient columns is saturation of the salt with respect to the uranium in the metal.

In the experiments to date, the uranium concentration of the salt reached at least 20 to 30% of equilibrium. Since the packed section was only 6 in. long and the salt phase was essentially stagnant, these results indicate that a countercurrent packed column would be a practical means of exchanging distributing solutes between liquid metals and salts. Before more definite conclusions are made, the experiments will be refined and will also be made with a rare earth as the transferring element.

d. Purification of Chloride Salts

For the advanced fuel recovery processes to be feasible, a practical method must be found for purifying relatively large quantities of chloride salts which are used in these processes. Untreated salts containing MgCl_2 are extremely corrosive toward all steels, contain large quantities of insolubles, and contain substances that react with UCl_3 to form UO_2Cl_2 and UO_2 . These undesirable properties are attributed to the difficulty of removing the last traces of water from MgCl_2 .

The objectives of an engineering-scale purification technique are (1) elimination of oxidizing substances which would attack structural materials, (2) removal of insoluble material that might interfere with the flow of fluids through equipment, and (3) removal of any substance that would form precipitates with uranium, plutonium, or rare earths. Laboratory work has been directed toward a purification method in which impure salt is contacted with a Cd-Mg alloy at 550-600°C and then filtered at temperatures between 450 and 500°C through a stainless steel filter having 20- μ pores. Batches of salt purified by this technique have been clear and colorless when molten and usually have contained less than 0.001 w/o water-insolubles and about 2000 ppm oxygen. This oxygen is believed to exist primarily as MgO , which would have no adverse effect on structural materials. No reliable analysis for low concentrations of water or OH^- ion in the purified salt is presently available, but an indication that the water or OH^- ion content is very low was provided by the fact that on further treatment of the salt with magnesium, an extremely small amount of hydrogen (~ 0.1 cc) was evolved. It remains to be determined whether UCl_3 will form stable solutions with the treated salt. Equipment is being assembled to treat approximately 50 kg of salt per batch.

e. Corrosion of Ferrous Alloys by Molten Metal-Halide Flux Systems

Corrosion of four ferrous alloys* -- types 304 and 405 stainless steel, type 2 1/4 Croloy, and type 1019 carbon steel -- has been investigated for Cd-Mg-Zn-U and halide flux systems which include compositions under consideration for use in the advanced core processes. These preliminary screening tests were conducted under static conditions at 600 and 650°C for 200 hr. The halide flux chosen for this work was 35 m/o NaCl-25 m/o LiCl-40 m/o MgCl₂ (m.p. about 475°C). The salt was dried by liquation at 600°C for 1 hr under a flowing argon atmosphere, a procedure which was later determined to be not completely effective. Corrosion results obtained are shown in Table I-6.

Both type 405 stainless steel and Croloy 2 1/4 withstood corrosive attack well at zinc concentrations of 10 w/o and less. Type 1019 carbon steel, although reasonably resistant to attack, was somewhat embrittled. Type 304 stainless steel underwent severe attack by nickel leaching by all liquid metals containing zinc, and clearly could not be used as a construction material. In general, corrosion rates were increased by increase in temperature and by increase in the zinc concentration of the metal alloy. Previous experience showed that the water content of the flux has a significant effect on corrosion rates, and it is believed that the corrosion rates could be reduced somewhat by using a more thoroughly dried salt.

Additional tests were made at 650°C for 200 hr to test further the corrosion resistance of type 405 stainless steel to a metal-flux system. In these tests the metal phase was composed of 81.4 w/o Cd-5.4 w/o Mg-10.9 w/o Zn-2.3 w/o U and the salt phase of 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl**. These experiments were conducted by attaching the specimens to a shaft rotating in the liquid media contained in an alumina crucible. One specimen was located in each of the liquid phases, one at the metal-salt interface, and one in the vapor phase. When the salt had been thoroughly purified

* Nominal alloy compositions (w/o) are as follows:

Alloy	Fe	Ni	Cr	C	Mn	Other
1019 Carbon Steel	98+	-	-	0.19	0.85	0.09
Croloy 2 1/4	95+	-	2.25	0.15	0.45	1.6
304SS	66+	8-11	18-20	0.08	2.0	1.1
405SS	82+	-	11-15	0.08	1.0	1.4

** The composition of the salt mixture used in these tests differed somewhat from that used in the previous tests. This is because the earlier tests were made before it was decided to use the 50 m/o MgCl₂-30 m/o NaCl-20 m/o KCl in the prototype extraction facility. Corrosion characteristics of the two salt mixtures should be similar.

Table I-6

CORROSION OF FERROUS ALLOYS BY Cd-Mg-Zn-U/
CHLORIDE FLUX SYSTEMS

Duration of Test: 200 hr

Static Conditions

Flux^a: 35 m/o NaCl

25 m/o LiCl

40 m/o MgCl₂

Metal Phase (w/o)				Temp (°C)	Maximum Observed Depth of Corrosion (mils)			
Zn	Mg	Cd	U		1019 Carbon Steel ^b	Croloy 2 1/4	304 SS	405 SS
0	80	20	0	600	2	0.4	1	<0.1
0	60	40	0	600	-	0.4	0.4	<0.1
0	40	60	0	600	<0.1	0.6	-	<0.1
15	10	72	3	600	0.4	0.4	2.5	0.4
15	15	67	3	600	<0.1	2	2	2
20	10	69	1	600	2	1	4	2
10	15	74	1	600	>2	0.5	5	0.5
15	10	72	3	650	1	2	5	0.5
15	15	67	3	650	2	1	6	2
20	10	69	1	650	>2	2	>12	2
10	15	74	1	650	>2	1	78	4

^a Flux dried by liquation in an argon atmosphere at 600°C for 1 hr.

^b Specimens were 4 mils thick. Values reported as >2 indicate corrosion across entire specimen thickness.

and dried by contacting it with a molten cadmium-magnesium alloy and filtering to remove oxide impurities, the corrosion rate for all test specimens was less than 1 mil in 200 hr. When the salt was allowed to take up some water by exposure to the atmosphere for about 1 hr, the rate of corrosion of the coupons in the salt and metal phases increased markedly, being greater than 5 mils in 200 hr for the test specimen in the vapor phase. It is evident that the water content of the salt flux influences the corrosiveness of the flux on ferrous alloys and that stringent measures will have to be used to produce and maintain a salt of low water content.

f. Oxidation Rates of Type 405 Stainless Steel and Croloy 2 1/4

Because type 405 stainless steel appears to have adequate corrosion resistance to salt-metal process systems and because uranium solutions are reasonably stable when contained in type 405 vessels, type 405 stainless steel has been chosen as the material of construction for the prototype extraction facility discussed in part a of this section. Unlike the eventual plant equipment which will be operated in an inert atmosphere (argon-5% nitrogen) in the EBR-II Fuel Cycle Facility, the experimental equipment will be operated in air at temperatures of about 600°C. Therefore, tests were performed to evaluate the oxidation resistance of type 405 stainless steel in air. Croloy 2 1/4 was also tested since it has shown some promise for containment of process solutions. For these tests, the sample metal was heated in air for 200 hr at 600°C for Croloy 2 1/4 and at 650°C for type 405 stainless-steel. After 200 hr, the specimens were cooled, and the amount of oxidation was determined by weighing the specimens. The samples were reheated for an additional 200 hr under identical conditions to determine if the oxide film previously formed would significantly limit further oxidation. Data obtained are shown in Table I-7. Type 405 stainless steel oxidized slightly in the first 200-hr period with no significant additional oxide formed during the additional 200 hr. Croloy 2 1/4 oxidized significantly during the first 200 hr, and although the rate was substantially less during the second 200 hr, significant oxidation rates still prevailed.

The superior air oxidation resistance of type 405 stainless steel reinforces the decision (based on its good corrosion resistance to molten metal and salt process solutions) to fabricate experimental process equipment from this material.

g. Performance of Silicon Carbide for Containment of Flux-Metal Systems

Two runs were conducted to evaluate oxynitride-bonded silicon carbide * crucibles for containing Zn-Mg/halide flux systems. In these tests,

* Crystalon 63, a product of the Norton Company, Worcester, Mass.

Table I-7

RESISTANCE TO AIR OXIDATION OF TYPE 405
STAINLESS STEEL AND CROLOY 2 1/4

Steel	Temp. (°C)	
	200-hr exposure	400-hr exposure
Croloy 2 1/4	+42.9	+54.0
Type 405 Stainless Steel	+ 0.11	+ 0.11

^a Values listed are each averages for 8 samples.

conducted at 900°C and 800°C, a silicon carbide crucible was subjected to a Zn-5 w/o Mg-2 w/o U/halide flux (CaCl_2 , MgCl_2 , CaF_2) system. After 48 hr of exposure, it was found that the flux had leaked through the crucible wall and collected in the secondary. No evidence of corrosion by the metal phase was evident. It is concluded that oxynitride-bonded silicon carbide is too porous for containment of halide fluxes.

h. Eddy Current Induction Probe for Liquid Level Measurements

Several types of instruments will be required for continuous processes, including devices to measure liquid flow rates, liquid levels, and pressures. The first instrument to be investigated is one to measure the level of metal in a tank and to detect the location of the metal-salt interface in extrac-tion devices. An accurate and reliable method of determining metal depths is required for continuous processes and is desirable for the batch processes currently being developed for the EBR-II fuel cycle. The development of a stationary eddy current induction probe for these measurements is nearly complete. The probe consists of a bifilar winding of nichrome wire placed around an alumina form and encased in a corrosion-resistant well which extends into the liquid. The circuit diagram for the probe is shown in Figure I-23. When a high-frequency voltage is applied to one coil, the voltage induced in the second coil is sensitive to the presence of an electrical conductor in the medium surrounding the coil, and therefore, to the depth of immersion of the coil in a liquid metal. The induced voltage is reduced as a result of the eddy currents induced in the liquid metal.

The use of a probe consisting of an alumina form made with two helical grooves to insulate the wires and to insure uniform coil spacing has eliminated completely the need for any insulating adhesive. Ceramic adhesives which were used in earlier work to hold the wires on an alumina rod proved to be unsatisfactory. One of the newer probes has given reproducible

Figure I-23

CIRCUIT DIAGRAM FOR EDDY CURRENT INDUCTION PROBE

readings (maximum deviation of $\pm 1/8$ in. of cadmium) over a three-month period, during which it was at temperatures above 350°C for more than 300 hr and was cycled between 700°C and room temperature at least 30 times. This probe had a maximum drift of 0.05 mv (equivalent to $1/32$ in. of cadmium) when it was held at 450°C for 16 hr. The drift caused by shutting down and restarting was $\pm 1/8$ in. It is believed that this reproducibility will be acceptable for most applications.

Typical calibration data for liquid cadmium are shown in Figure I-24. The probe was placed in a stainless steel well (0.032-in. wall) with the bottom of the well resting on the bottom of a stainless steel crucible. The position of the probe was kept constant since the location of the crucible bottom with respect to the coil was found to influence the output signal slightly. The depth of liquid metal was changed by adding increments of cadmium. The metal-gas interface was located with a resistance probe.

The signal from the eddy current induction probe is a function of temperature because of the change in the resistances of the nichrome wire, the well, and the liquid metal with temperature. This temperature coefficient had a slight dependence on the melt depth, which would be negligible for most applications, and could be conveniently corrected by changing the bias or bucking voltage, as shown in Figure I-25, to make the isotherms of Figure I-24 coincide with a 550°C curve. The bias voltage was subtracted from the rectified output signal to shift it to values which

Figure I-24

EFFECT OF MELT DEPTH ON OUTPUT SIGNAL OF EDDY CURRENT
LIQUID-LEVEL PROBE

Input Frequency: 50,000 cycles/sec
Oscillator Voltage: 7.0 volts
Bias Voltage: 4.64 millivolts

Crucible: 304 SS, 10 in. high by 5 5/8-in. ID
Liquid Metal: Cadmium
Length of Winding: 5 1/8 in.

Figure I-25

TEMPERATURE COMPENSATION FOR LIQUID LEVEL PROBE

Corrections to bias voltage required to use 550°C calibration isotherm at another temperature

Liquid Metal: Cadmium
 Crucible: 304 SS, 10-in. high by 5 5/8-in. ID
 Well: 304 SS, 32-mil wall
 Length of Winding: 5 1/8 in.

could be recorded conveniently.

The high-frequency coils were relatively insensitive to the geometry of the surroundings because of the small depth of penetration of the induced eddy currents. For materials having resistivities of the order of 10-100 $\mu\text{ohm-cm}$, the calculated effective depth of penetration is less than 3/8 in. if the input frequency is 50 kc. Stainless steel crucibles having inside diameters greater than 1 1/2 in. had no detectable effect on the output signal. Therefore, a probe calibration made in one geometry should be applicable to other situations.

The probe can detect the presence of any fluid having a high electrical conductivity. The presence of a molten salt, composed of either 50 m/o MgCl_2 - 30 m/o NaCl - 20 m/o KCl or 50 m/o MgCl_2 - 50 m/o CaCl_2 , had no detectable effect on the output signal. These salts have low conductivities compared with liquid metals. Therefore, in a two-phase system, only the salt-metal interface would be detected. When the probe was calibrated in liquid bismuth, the change in signal with change in liquid depth was somewhat smaller than for cadmium. This would be expected because the resistance of bismuth is about four times higher than that of cadmium.

For the measurement of liquid levels in systems containing volatile, corrosive molten metals, the eddy current induction probe has proved to be superior to any other type of liquid level instrument investigated, including those devices which depend on electrical resistance, hydrostatic pressure, or position of a float. The induction probe has been reliable, its readings are reproducible, and it has an accuracy of $\pm 1/8$ in., which is acceptable for most applications. The instrument should be easily adaptable to remotely operated high temperature equipment since it has no moving parts. Future work will be directed toward the application of the

Figure I-26

LIQUIDUS TEMPERATURES FOR THE SYSTEM LiCl-KCl-MgCl_2

Figure I-27

LIQUIDUS TEMPERATURES FOR THE SYSTEM LiCl-NaCl-MgCl_2 .Temperatures in $^{\circ}\text{C}$.

instrument to specific process equipment.

C. Supporting Chemical Studies

1. Chemistry of Molten Salts

Since molten salt solutions are utilized in various compact pyrochemical processes, fundamental chemical studies of molten chloride systems are being conducted to provide supporting data for process use.

a. Liquidus Temperatures of Ternary Salt Systems

In the present conceptual processes for fast breeder reactor fuels, low-melting mixtures of alkali metal chlorides and MgCl_2 are used for the extraction of electropositive fission product elements from liquid metal solutions of uranium and plutonium. Low-temperature operation is desirable in this step in order to increase the efficiency of the separation and to decrease the corrosion rate of the process vessels. Liquidus temperatures of the ternary systems, LiCl-NaCl-MgCl_2 and LiCl-KCl-MgCl_2 , have therefore been determined. Temperature-composition diagrams based on thermal analysis

data are shown in Figures I-26 and I-27. The minimum liquidus temperatures observed were 433°C at 5.5 m/o LiCl-59.5 m/o NaCl-35.0 m/o MgCl₂ and 336°C at 40 m/o LiCl-50 m/o KCl-10 m/o MgCl₂. At MgCl₂ concentrations above about 50 m/o, which are required for satisfactory extraction of rare earth fission products, both systems possess sufficiently low melting temperatures (below about 550°C) for process use.

b. Ion Exchange in Molten Salt Solvents

The possibility of purifying process salts for recycle by extracting fission product elements with inorganic ion exchange media has been explored briefly. In all of the studies, "Tipersul"* (potassium hexatitanate) was used as the solid ion exchange medium. Mixtures of KBr and AlBr₃ in varying proportions were used as the solvent in the initial studies, and Ba⁺² at a concentration of about 0.01M was the exchanging ion. For analytical convenience, the

Table I-8

ION EXCHANGE IN MOLTEN SALT SOLUTIONS

Solid Phase: potassium hexatitanate ("Tipersul")

<u>Salt Composition</u>	<u>Exchange Ion</u>	<u>Temperature (°C)</u>	<u>Distribution Coefficient, Kd^a</u>
20 m/o KBr-80 m/o AlBr ₃	Ba ⁺² , 0.013M	140	~0
33 m/o KBr-67 m/o AlBr ₃	Ba ⁺² , 0.012M	140	~0
43 m/o KBr-57 m/o AlBr ₃	Ba ⁺² , 0.011M	180	~0
50 m/o KBr-50 m/o AlBr ₃	Ba ⁺² , 0.010M	220	10 ³ -10 ⁴
55 m/o KBr-45 m/o AlBr ₃	Ba ⁺² , 0.010M	550	8
100 m/o AlBr ₃	U ⁺⁴ , 0.06M	140	~0
50 m/o KBr-50 m/o AlBr ₃	U ⁺⁴ , 0.016M	220	16
100 m/o KNO ₃	Ba ⁺² , 0.010M	370	540
30 m/o NaCl-20 m/o KCl- 50 m/o MgCl ₂	Ba ⁺² , 0.015M	450	6

$$^a \text{Kd} = \frac{^{133}\text{Ba activity/g solid}}{^{133}\text{Ba activity/g salt}} \quad \text{or} \quad \frac{\text{w/o U in solid}}{\text{w/o U in salt}}$$

* A product of E. I. duPont de Nemours and Co., Inc.

Ba^{+2} was spiked with ^{133}Ba tracer and the samples were analyzed by gamma counting. Distribution coefficients, defined as $(\text{cpm/g solid})/(\text{cpm/g solution})$, were determined by counting filtered samples of the salt before and after contact with the Tipersul. The results are listed in Table I-8. Low distribution coefficients (0 to 8) were observed when the $\text{KBr}:\text{AlBr}_3$ mole ratio was different from unity, but in equimolar $\text{KBr}-\text{AlBr}_3$, high distribution coefficients (10^3 to 10^4) were obtained. A reverse experiment, with the barium activity initially on the Tipersul and using equimolar $\text{KBr}-\text{AlBr}_3$ as the salt, resulted in approximately the same distribution coefficient (4×10^3).

The same general effect of solvent composition was noted when U^{+4} instead of Ba^{+2} was used as the exchanging ion. However, the distribution coefficient in equimolar $\text{KBr}-\text{AlBr}_3$ had a much lower value (~ 16) than that obtained with Ba^{+2} . Two other molten salt solvents were examined briefly with Ba^{+2} as the exchanging ion. In molten KNO_3 at 370°C , the distribution coefficient was 540, and in the ternary eutectic, $\text{NaCl}-\text{KCl}-\text{MgCl}_2$ at 450°C , a value of 6 was obtained. The ternary eutectic is typical of salt systems used in fuel processing, and therefore, this latter result is of particular interest, as it suggests that this technique may permit the removal of electropositive fission products such as rubidium, cesium, strontium, and barium from salt effluents. The purified salts could then be reused.

2. Substitution of Cadmium and Magnesium for Zinc in U_2Zn_{17}

Data on the solubility of uranium in liquid cadmium-magnesium-zinc alloys were presented in a previous report (ANL-6875, p. 26). Over a range of solution compositions and temperatures, the delta-phase uranium-zinc intermetallic compound, U_2Zn_{17} , was identified as the solid phase in equilibrium with the saturated solution. Subsequent X-ray data and chemical analyses have shown that small amounts of cadmium and magnesium can be substituted for zinc in U_2Zn_{17} without changing the basic crystal structure when the compound is precipitated from cadmium-magnesium-zinc solutions. The data, shown in Table I-9, indicate that the degree of cadmium and magnesium substitution is essentially independent of the solvent composition over the range that was investigated. However the lattice parameters, a and c , of the hexagonal structure both show an increase that is roughly proportional to the cadmium and magnesium content of the U_2Zn_{17} (see Figure I-28). Pertinent metallic radii given by Pauling⁵ are as follows: Zn, 1.379 Å; Cd, 1.543 Å; Mg, 1.598 Å. The observed behavior appears to be in qualitative agreement with the interpretation that cadmium and a small amount of magnesium can be substituted for those zinc atoms that lie above and below the planes of the hexagonal structure, but not for those that form the planes.

⁵ Pauling, L., J. Am. Chem. Soc. 69, 542 (1947).

Table I-9

CADMIUM AND MAGNESIUM SUBSTITUTION IN U_2Zn_{17} PRECIPITATED
FROM CADMIUM-MAGNESIUM-ZINC SOLUTIONS

Solution Composition (a/o)			Composition of Precipitated Phase (atom ratios)				Lattice Parameters (Å)	
<u>Zn</u>	<u>Cd</u>	<u>Mg</u>	<u>Zn:U</u>	<u>Cd:U</u>	<u>Mg:U</u>	<u>(Zn+Cd+Mg):U</u>	<u>a</u>	<u>c</u>
30	60	10	7.65	0.39	0.06	8.10	9.0215	13.2286
20	60	20	7.98	0.40	0.11 ^a	8.49	9.0239	13.2296
20	67	13	8.13	0.39	0.04	8.56	9.0204	13.2205
20	70	10	8.16	0.29	0.03	8.48	8.9998	13.1875
13	74	13	7.80	0.52	0.04	8.36	9.0306	13.2358
13	77	10	7.74	0.71	0.03	8.48	9.0345	13.2428
10	80	10	7.97	0.71	0.05	8.73	9.0359	13.2423
7	77	16	8.18	0.48	0.03	8.69	9.0252	13.2226
6	74	20	8.35	0.34	0.03	8.72	9.0187	13.2181
Pure U_2Zn_{17}			8.50	0	0	8.50	8.9810	13.1610

^a Questionable value.

Figure I-28

EFFECT OF CADMIUM AND MAGNESIUM SUBSTITUTION ON LATTICE PARAMETERS OF U_2Zn_{17}

A preliminary determination of the miscibility gap has been made by equilibrating the two liquid phases at various temperatures, withdrawing samples of each phase, and analyzing the samples for plutonium. A tentative

3. Plutonium-Magnesium Phase Diagram

The phase diagram of the binary system, plutonium-magnesium, is of practical importance in the plutonium recovery operations associated with the EBR-II Blanket Process. Although the general features of this phase diagram and the presence of two immiscible liquid phases were indicated by earlier work at Los Alamos,⁶ the region of immiscibility was not defined. The objective of the present study is to determine the immiscibility curve as a function of temperature and composition and to confirm the liquidus temperatures outside the miscibility gap.

Figure I-29

LIQUID MISCIBILITY GAP IN THE SYSTEM PLUTONIUM-MAGNESIUM

⁶ Schonfeld, F. W. et al., "Plutonium Constitutional Diagrams" in Metalurgy and Fuels, H. M. Finniston and J. P. Howe, Eds., Progr. in Nuclear Energy, Series V, Vol. 2, Pergamon Press, New York, 1959, p. 579.

diagram of the miscibility gap based on these data is shown in Figure I-29. At 625°C the region of immiscibility extends from about 8.5 to 84 a/o magnesium. The consolute temperature appears to be about 975°C . Work is continuing on this system in an effort to confirm the immiscibility curve by an independent method, and to determine the liquidus curves outside the miscibility gap by thermal analysis.

D. Supporting Engineering Studies

1. Determination of Critical Constants of Alkali Metals

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

Figure I-30

HIGH PRESSURE CELL FOR MEASUREMENT OF CRITICAL TEMPERATURE OF ALKALI METALS

properties of alkali metals are of particular interest because of their use as heat-exchange media in nuclear reactors. While many estimates have been made of the critical constants of alkali metals, no actual measurements of the critical constants, vapor pressure, vapor density, and liquid density are known for the entire range of temperature from the boiling point to the critical point. Therefore, measurements are being made of vapor and liquid density as a function of temperature for the alkali metals sodium, potassium, rubidium, and cesium from room temperature up to or as close as possible to the critical point. Densities are being determined by measurement of gamma radiation emanating from the liquid and vapor phases of radioactive tracer-containing metal held in a high-pressure capsule. As the critical point is approached, the densities of the two phases and therefore the gamma activities emanating from the vapor and liquid phase regions approach each other.

Early studies were made using the three-piece configuration and furnace assembly shown in Figures I-30 and I-31. With this equipment, density data have been obtained for rubidium and cesium up to near the critical temperatures.

Figure I-31

FURNACE ASSEMBLY FOR CRITICAL TEMPERATURE APPARATUS

Figure I-33

DETERMINATION OF THE CRITICAL TEMPERATURE OF RUBIDIUM

Estimated $T_c = 1820^\circ\text{C}$
 Estimated $\rho_c = 0.35 \text{ g/cc}$

For rubidium the estimated critical temperature is about 1820°C based on data up to 1720°C . These data are shown in Figure I-32. The estimated critical temperature for rubidium is somewhat lower than the estimate of Grosse⁷ (1917°C) and somewhat higher than the extrapolation of Hochman and Bonilla⁸ (1727°C). The corresponding density at 1820°C is 0.35 g/cc and is consistent with the known volume of the capsule and the amount of material charged. It compares favorably with Grosse's estimate⁷ of 0.32 g/cc at 1917°C critical temperature.

The data for cesium are shown in Figure I-33. Extrapolation of the experimental data, which were obtained up to a temperature of 1635°C , gives a critical temperature of about 1850°C . This is close to Grosse's estimate⁷ of

⁷ Grosse, A. V., The Liquid Range of Metals and Some of Their Physical Properties, USAEC Report NP-10795, Sept. 5, 1960.

⁸ Hochman, J.M. and C.F. Bonilla, The Electrical and Thermal Conductivity of Liquid Rubidium to 2900°F . J. Electrochemical Society, 111, 200C (August 1964). Also Extended Abstracts of Electrothermics and Metallurgy Division, The Electrochemical Society, Inc., Fall Meeting, Washington, D.C., Oct. 11-15, 1964, 2, No. 2, p. 58.

1887°C but considerably above the 1783°C estimated by Hochman and Bonilla.⁹ The corresponding density at 1850°C is 0.40 g/cc. This value also compares favorably with Grosse's estimate⁷ of 0.42 g/cc at 1887°C critical temperature.

Additional runs will be made in the improved design configuration shown in Figure I-34. The salient new feature is the split tapered center piece held in place by a 3-in. OD taper sleeve. This design will have greater strength and is designed to eliminate galling and seizing encountered with the three-piece design which made the removal of both the threaded plugs and the capsule difficult. The additional runs will include ones made to firm up and make more complete the data on cesium and rubidium. Vapor and liquid densities of sodium and potassium will also be measured to as high a temperature as possible.

Figure I-32

DETERMINATION OF THE CRITICAL TEMPERATURE OF CESIUM

Estimated $T_c = 1850^\circ\text{C}$
Estimated $\rho_c = 0.40 \text{ g/cc}$

⁹ Hochman, J. M. and C. F. Bonilla, The Electrical and Thermal Conductivity of Liquid Cesium to 3000°F, and the Critical Point of Cesium Trans. Am. Nucl. Soc. 1, 101 (June 1964).

Figure I-34

REVISED FURNACE ASSEMBLY FOR CRITICAL TEMPERATURE APPARATUS

- 1, Insulation
- 2, 1/4-in. tantalum tubes connecting to temperature measurement holes in tapered Mo-30 w/o W cylinder
- 3, Fiberfrax lid
- 4, Tantalum can and lid
- 5, Tapered Mo-30 w/o W cylinder in 3-in. OD Mo-30 w/o W sleeve
- 6, Locating pin
- 7, Mo-30 w/o W capsule containing alkali metal in 3/16-in. ID narrow section 1-in. long by 30-mil wall
- 8, Locating pin
- 9, Silicon carbide crucible (6 1/2-in. OD x 11 in. high x 1/2-in. wall)
- 10, 1/4-in. tantalum tubes connecting to collimation holes in Mo-30 w/o W cylinder
- 11, 1/2-in. "Veeco" fittings in wall of vacuum tank

2. Determination of Viscosities of Liquid Metals and Fused Salts

The viscosity of certain liquid metal and liquid salt solutions is of interest in interpreting mass transfer and fluid dynamics results in some of the compact pyrochemical processing studies. For this reason, apparatus has been constructed for the determination of these viscosities. The equipment consists of a cup suspended by a torsion wire and instrumentation to measure the damping of the rotational oscillations of the cup by the viscous shear of the fluid under study, which is contained in the cup. The major advantages of the selected method are (1) high sensitivity resulting from an extended period of viscous damping, (2) relatively small sample size, and (3) lack of a requirement for direct observation of the fluid. The cup is suspended in a furnace with only an extension visible for amplitude and period of oscillation measurements.

Several mathematical relationships have been determined relating the

parameters of the viscometer to the viscosity of the contained liquid. These formulations allow calculation of the viscosity of a measured fluid either from the parameters of the system directly or from a calibration of the instrument with a fluid of known viscosity.

Construction of the viscometer has been completed. Preliminary measurements have been made on mercury and on cadmium-base alloys.

3. Measurement of the Surface Temperature of a Liquid Metal during Vaporization

During studies now completed of the nonturbulent vaporization of mercury (see previous reports ANL-6875, p. 41, and ANL-6766, p. 39), a surface thermocouple was devised for the surface temperature measurement and was employed to obtain temperature patterns of the mercury surface. The measurement of the temperature of a liquid surface undergoing vaporization is difficult because of the steep temperature gradient in the liquid near the surface, and, therefore, the development of a thermocouple for direct measurement of surface temperatures is noteworthy. The thermocouple consisted of a 10-mil bare chromel wire which dipped into the liquid metal surface from the vapor space. The mercury itself was one leg of the thermocouple. From a theoretical analysis of factors affecting the accuracy of temperature measurements made by the surface probe, the error in temperature measurement was estimated to be less than 1°C under the experimental conditions utilized. The mathematical analysis can be used for the design of future probes with specified accuracy.

E. Chemistry of Liquid Metals

The chemistry and thermodynamic properties of liquid metal systems and metallic alloys are being investigated to provide basic data for the pyrochemical processing of nuclear fuels and for liquid alkali metal technology. The results of these studies also provide data for the testing of theories of liquid metal solutions.

1. Thermodynamic Studies

a. Thermodynamics of Lanthanum-Cadmium Systems

The thermodynamics of the lanthanum (rare earth metals) - cadmium (Ln-Cd) systems are being investigated for two principal reasons. (1) A key step in the purification of spent nuclear fuels is the separation of the lanthanum metals from the actinide metals, especially plutonium (see Section IB3); thus, knowledge of the thermodynamic properties of the lanthanons in potentially useful metallic solvents is extremely useful for the design of separation processes. (2) From the theoretical point of view, the lanthanum-cadmium systems offer the possibility of investigating several

important aspects of alloy thermodynamics.

The constancy of the electronegativities (~ 1.2) and valencies (3) in combination with the gradual decrease in atomic radius in progressing from the light to the heavy lanthanons permits the isolation of the influence of atomic size on intermetallic compound stability. The existence of two exceptional lanthanons, europium and ytterbium, with lower electronegativities (~ 1.0) and valencies (2) than the rest, allows a partial resolution of the combined effects of atomic size, electronegativity, and valency on intermetallic compound stability.

Two experimental methods are employed in these studies. (1) High-temperature galvanic cells are used to measure activities in liquid metal solutions and to determine the free energies of formation of the solid cadmium-rich intermetallic phases (LnCd_{11} compounds) in equilibrium with liquid cadmium solutions. (2) The Knudsen effusion method is used to measure the decomposition pressures of systems composed of several well-defined intermetallic phases. The free energies of formation of the complete series of stable compounds for a representative number of Ln-Cd systems are being determined. The two experimental methods complement each other.

(i) Galvanic Cell Studies

Thermodynamic data obtained for LnCd_{11} intermetallic compounds are summarized in Table I-10. The negative free energies of formation, $-\Delta G_f^\circ$, decrease from LaCd_{11} to NdCd_{11} ; likewise, the negative ideal free energies of solution, $-RT \ln x_{\text{Ln}}$, also decrease with increasing atomic number of the lanthanon. The variation in the free energy of formation may be understood by consideration of the crystalline structure of the LnCd_{11} compounds and the lanthanide contraction. The LnCd_{11} compounds may be considered as built up from cadmium polyhedrons in whose centers are the lanthanon atoms. The dimensions of the crystal lattice are principally determined by the cadmium polyhedrons. The average radius of the polyhedral cavity in which the lanthanon atom must fit varies by less than one percent between LaCd_{11} and SmCd_{11} , whereas the radius of the lanthanon atom decreases by either 4 or 10 percent depending on whether one considers metallic or ionic radii. Consequently, the fit of the lanthanon atom becomes progressively poorer from LaCd_{11} to SmCd_{11} . This leads to less negative enthalpies of formation (the atomic binding is weaker) and to less negative entropies of formation (the absolute entropies of the compounds increase owing to lower lattice vibrational frequencies).

The solubility of a given lanthanon in liquid cadmium is influenced by both the free energy of formation of the equilibrium solid phase $[\Delta G_f^\circ(\text{LnCd}_{11})]$ and the partial molar excess free energy ($\bar{G}_{\text{Ln}}^{xs}$) of the solute in solution; the relationship is given by the equation

$$RT \ln x_{\text{Ln}} = \Delta G_f^\circ - \bar{G}_{\text{Ln}}^{xs}$$

Table I-10

THERMODYNAMIC PROPERTIES OF LnCd_{11} COMPOUNDS (400°C) $(x_{\text{Ln}}$ = atom fraction solubility of lanthanon in liquid cadmium^a)

Compound	$-\Delta H_f^\circ$ (kcal/mole)	$-\Delta S_f^\circ$ (cal/deg mole)	$-RT \ln x_{\text{Ln}}$ (kcal/mole)	$-\Delta G_f^\circ$ (kcal/mole)	$-\bar{G}_{\text{Ln}}^{xs}$ (kcal/mole)
LaCd_{11}	72.9	44.3	11.3	43.1	31.8
CeCd_{11}	71.2	45.6	10.3	40.5	30.2
PrCd_{11}	69.0	44.7	9.5	39.0	29.5
NdCd_{11}	63.5	38.8	8.7	37.4	28.7
PmCd_{11}	-	-	-	-	-
SmCd_{11}	-	-	6.7	-	-

^a For solubilities see: I. Johnson, Solubility of the Rare Earth Metals in Liquid Cadmium, in Rare Earth Research, edited by J. F. Nachman and C. E. Lundin, Gordon and Breach, New York, N. Y., 1962, pp. 125-131.

where x_{Ln} is the atom fraction solubility of Ln in liquid cadmium. Inspection of Table I-10 shows that the increase in solubility of the lanthanons as their atomic number increases is due to the more rapid decrease of the $-\Delta G_f^\circ$ terms than of the $-\bar{G}_{\text{Ln}}^{xs}$ terms. This seems reasonable since the size requirements of the liquid cadmium quasi-lattice are probably not as rigid as those of the LnCd_{11} lattice.

(ii) Effusion Studies

Prior to this report period, single pressure-composition (effusion) isotherms were determined for each of 11 of the 14 Ln-Cd systems (e.g., see ANL-6725, p. 110). These data established the number of intermetallic compounds present in each system, their approximate stoichiometries, and their relative stabilities. Currently, the standard free energies of formation of all the intermetallic compounds in selected Ln-Cd systems are being obtained by the determination of the partial molar free energy of cadmium in each solid two-phase region of the phase diagram.

Optimum experimental conditions for the determination of decomposition pressures of Ln-Cd systems by the Knudsen effusion method

are realized when the alloy sample is solid and the partial pressure of cadmium is in the range 0.001 to about 1 torr. In order to ensure the presence of solid alloys for effusion experiments in the LnCd-Ln fields, upper temperature limits, namely, the eutectic temperatures, were determined by differential thermal analysis. The results for eight LnCd-Cd systems are given in Table I-11. Except for lanthanum, europium, and ytterbium, all of which would be expected to show anomalous behavior, the eutectic temperatures increase with increasing atomic number (and melting point of the lanthanon metal). If this trend continues, the eutectic temperatures for the remaining LnCd-Ln systems will be high enough to permit effusion measurements to be made under satisfactory temperature and pressure conditions.

Table I-11

EUTECTIC TEMPERATURES IN THE LnCd-Ln
REGIONS OF THE LANTHANON-CADMIUM SYSTEMS

<u>System</u>	<u>Eutectic Temperature (°C)</u>
La-Cd	476
Ce-Cd	417
Pr-Cd	435
Nd-Cd	486
Sm-Cd	554
Eu-Cd	439
Gd-Cd	719
Yb-Cd	458

The decomposition pressures of SmCd, GdCd, TmCd, and LuCd have been measured and are shown as a function of temperature in Figure I-35. The free energy of formation of the LnCd intermetallic compound is related to the decomposition pressure, p , by the equation

$$\Delta G_f^0 = RT \ln (p/p_0),$$

in which p_0 is the partial pressure of pure cadmium at the temperature T . Hence, the stabilities decrease in the order: GdCd, SmCd, TmCd, LuCd. This is also the order of decreasing metallic radii for these lanthanon metals.

Figure I-35

DECOMPOSITION PRESSURES OF GdCd, SmCd, TmCd, and LuCd

b. Thermodynamics of Binary Alkali Metal Solutions

The formulation of an adequate theory of metallic solutions has been slow. The electron theory of metals has not provided a clear understanding of the thermodynamic properties of even simple metallic solutions. Recent interest in the application of many-body theory to metallic solutions has shown the need for experimental data on such simple metallic solutions as those of the alkali metals. A study was undertaken to measure the thermodynamic properties of selected binary liquid alkali metal systems.

The components of these systems have appreciable vapor pressures, but only small differences in electrochemical potential. Thermodynamic properties are being obtained by vapor phase absorption spectrophotometry in which light of characteristic frequency (resonance radiation) is passed through the vapors above either a pure alkali metal or its alloys. The quantity of resonance radiation which is absorbed is a measure of the concentration of an alkali metal in the vapor. Comparison of the absorption by an alloy to that by

a pure alkali metal is, in principle, a direct measure of the thermodynamic activity of that metal in the solution.

The thermodynamic activity of sodium in several liquid Na-K solutions was determined in the range 135 to 150°C. Over this short range, no temperature variation of the activity outside of the expected experimental error could be observed. Therefore, the results are given in a single figure, Figure I-36, which shows the variation of the sodium activity with solution composition. It is evident that sodium and potassium form solutions which exhibit positive departures from ideality.

A clearer exhibition of the thermodynamic properties of the Na-K system is shown in Figure I-37. On this plot are given the Gibbs excess free energy of mixing, ΔG^{xs} (derived by a Gibbs-Duhem integration of the present

Figure I-36

VARIATION OF SODIUM ACTIVITY
IN SODIUM-POTASSIUM
SOLUTIONS AT 414°K

Figure I-37

THERMODYNAMIC FUNCTIONS FOR
THE SODIUM-POTASSIUM SYSTEM
AT 414°K

results), the heat of mixing, ΔH^M (measured ¹⁰ at 111°C but assumed to be valid at 141°C), and the excess entropy of mixing (from $T\Delta S^{xs} = \Delta H^M - \Delta G^{xs}$). Inspection of Figure I-37 shows that even for this very simple system (1) the curves of ΔG^{xs} and ΔH^M vs. atom fraction are asymmetric, and (2) except for dilute solutions of potassium in sodium, the system is not regular, i.e., $\Delta S^{xs} \neq 0$. Tentative conclusions have been drawn from the data; namely, that the size effect may predominate over the electronic effect in this system, and that calculations involving both may be required to fit the data.

2. Liquid Sodium Chemistry

The increasing use of liquid alkali metals as heat exchange and working fluids in fast nuclear reactors and other power sources underlies the current fundamental research on the chemistry of reactions in liquid alkali metals. Special emphasis is being given to liquid sodium because its practical importance is greatest.

Sodium of known, high purity is needed for significant research. Studies are being made in the closely related areas of purification, analysis, and contamination during handling. Three common contaminants in sodium -- oxygen, hydrogen, and carbon -- appear to be particularly important with

¹⁰ Yokokawa, T., and O. J. Kleppa, J. Chem. Phys. 40, 46 (1964).

regard to its corrosive properties. An understanding of the major reactions involving these contaminants in liquid sodium will furnish a basis for a better understanding of corrosion mechanisms and possibly lead to new methods for corrosion control.

a. Sodium Analysis

(i) Oxygen

Sodium is being analyzed for total oxygen by a fast-neutron activation method (ANL-6875, p. 59) which involves the reaction $^{16}\text{O}(n,p)^{16}\text{N}$. A major obstacle to the realization of this method was the requirement of encapsulating the sample with a material which did not interfere because of its own oxygen content. Three encapsulation materials were examined: 2S aluminum, OFHC (oxygen-free high conductivity) copper, and polyethylene.

Capsules made of 2S aluminum had blanks equivalent to 10 to 30 ppm of oxygen. After repeated irradiation (to obtain adequate counting statistics for samples low in oxygen) and counting of the aluminum capsules, no appreciable buildup of long-lived activity was found within the energy range used for counting ^{16}N . There is reason to believe that if capsules were made of aluminum which has been vacuum liquated and bottom poured, the oxygen content would be low enough to permit analysis of sodium samples containing ≥ 10 ppm oxygen.

Capsules made from OFHC copper indicated oxygen contents equivalent to about 30 ppm. However, a long-lived activity which counted in the same energy range as ^{16}N built up after repeated irradiations. The impurity in copper responsible for this induced activity was not identified.

In the case of polyethylene, a decrease in the oxygen blank was sought by irradiation of the sodium at one end of an 8-in. long polyethylene tube and transfer of the sodium to the other end for counting. The decrease found, however, was inadequate. Both the polyethylene- and copper-encapsulation techniques were abandoned after finding that 2S aluminum capsules gave significantly lower oxygen blanks.

Routine analysis for oxygen in sodium by fast-neutron activation has been turned over to the Chemistry Division. With the present equipment, oxygen contents of ≥ 50 ppm can be determined satisfactorily. Improvements in the equipment are expected to bring this level down to 10 ppm.

(ii) Carbon

Various current studies required a method for the determination of carbon in sodium. Several analytical methods which were recently

tested¹¹ in a cooperative study by various laboratories gave highly scattered results. It is not clear whether the results afford a valid comparison of the analytical methods or, in fact, reflect differences attributable to variations in sampling and sample preparation techniques. In the light of this uncertainty, it was felt necessary to pursue further the problem of reliability of analytical and sampling techniques.

Most of the analytical techniques described in the literature¹²⁻¹⁵, are based on the oxidation of carbon to carbon dioxide and subsequent measurement of the quantity of evolved gas. The principal variations occur in the oxidant used and the method of liberating and measuring carbon dioxide. Our analytical investigations have employed the so-called "dry" oxidation method in which the sample of sodium is first burned in low-pressure (150 torr), ultra-pure oxygen to form a residue of mixed sodium oxide and sodium carbonate. The sample of sodium is loaded into a combustion tube in a helium-filled glovebox to avoid exposure of the sample to air. Two methods for liberating the carbon dioxide from the residue have been tested:

- (1) The residue is heated in a silica boat to 1100°C in oxygen. The carbon dioxide liberated by the reaction of sodium carbonate and silica is collected in a cold trap (liquid oxygen coolant) and subsequently measured manometrically. Reagent blanks of 4 µg or less have been consistently obtained.
- (2) The residue is treated with dilute sulfuric acid to liberate carbon dioxide which is then measured by gas chromatographic techniques. The reagent blanks in this method have consistently run 1.5 to 2 µg.

A comparison of the two methods was made using samples withdrawn from a pot of liquid sodium over a short interval of time. The results of this comparison are shown in Table I-12. The fairly good agreement between the average results of the two methods indicates their general equivalence. However, the rather large spread of apparent carbon contents points to the likelihood that there is a sampling problem. This problem is further discussed in Part c.

b. Sodium Purification

Ultrapure sodium is needed for the development of analytical

-
- ¹¹ R. W. Lockhart et al., Results of the USAEC Round-Robin Analysis for Carbon Impurity in Sodium, GEAP-4602, March 1964.
 - ¹² Pepkowitz, L. P. and J. T. Porter, II., KAPL-1444, Nov. 28, 1955.
 - ¹³ Herrington, J., AWRE-O-62/62, November 1962.
 - ¹⁴ Kallman, S. and R. Liu, Anal. Chem., 36, 590 (1964).
 - ¹⁵ Mungall, T. G., J. H. Mitchen, and D. E. Johnson, Anal. Chem., 36, 70 (1964).

Table I-12

APPARENT CARBON CONTENTS OF LIQUID SODIUM
AT 158°C BY THE "DRY" OXIDATION METHOD

High Temperature Reaction (ppm)	Acidification Reaction (ppm)
88	47
106	87
55	112
71	48
72	62
63	
Average 76 $\pm$ 18	71 $\pm$ 27

procedures and for the studies of reactions of liquid sodium with oxygen, hydrogen, and carbon. Methods now being examined for the purification of sodium include vacuum distillation, centrifugation, zone refining, filtration, and hot gettering.

Vacuum distillation has been frequently mentioned in the literature as the method of choice. Our experience with vacuum distillation, using a stainless steel still, indicated that metallic impurities were removed but that carbon contents below about 50 ppm were not achieved. Construction of a still with improved design is now under consideration.

Carbonaceous particulate matter capable of passing through a 5- μ -porosity filter has been found in all samples of sodium that we have examined. (Such particles may also be entrainable in distillation.) Centrifugation has not been previously applied to sodium purification but may be beneficial for carbon removal. Calculations indicate that particles larger than 1 μ should be separable by centrifugation at reasonable speeds and temperatures. A high-temperature centrifuge (500°C. maximum) has been constructed to test this concept.

Zone refining of sodium has not been reported in the literature, although the technique has been used extensively for the purification of other metals. In principle, the method depends on the difference in solubility of an impurity between the solid and liquid phases of the material being refined. Zone refining may also provide removal of particulate impurities by segregation to a moving liquid-solid interface. Simple zone refining equipment has been ordered to test the feasibility of purifying sodium by this technique.

Porous filters made of stainless steel, quartz, and other materials are being tested for removal of carbonaceous particulate matter from liquid

sodium. Results obtained to date indicate that these particulates are sub-micron-sized.

Experiments to test removal of impurities by hot gettering have only recently gotten under way. The first getters to be tried are calcium and Zr-15 w/o Ti alloy.

c. "Solubility" of Carbon in Liquid Sodium

It has been established that various metals may be significantly carburized or decarburized when in contact with liquid sodium. This phenomenon presents a potentially serious problem relative to the use of liquid sodium in nuclear reactors. Undesirable changes in the mechanical properties of structural materials, such as steel, may result from small changes in carbon content.

Various mechanisms of carbon transport have been proposed in the literature but the problem remains unresolved. A study of the transport of carbon in sodium must commence with understanding the chemical nature of carbon in sodium. The present study has been directed toward the determination of whether or not a true solubility of carbon in sodium exists.

Liquid sodium was held in contact with graphite under a helium atmosphere at various temperatures. Filtered samples were taken by pressurizing the liquid phase into tantalum tubes fitted with 5- μ -porosity stainless steel frits. The samples were transferred to the analytical apparatus without exposure to the atmosphere and analyzed for carbon by the high temperature "dry" oxidation method. All the individual analyses of replicate experiments are given in Table I-13. Noticeable in the data are their tendency to scatter erratically. There does not seem to be any significant increase in carbon content with temperature. These results suggested that the original sodium contained carbonaceous particulate matter capable of passing through a 5- μ -porosity stainless steel filter.

To check the particulate hypothesis, graphite which had been pulverized in the dry box was intentionally added to sodium in a graphite crucible and the previous experiment was repeated at a constant temperature of 316°C. The results were revealing. Although the starting sodium (sampled as a solid) had a carbon content of 220 ppm, the first filtered sample obtained after eight days of contact, one hour of stirring, and one hour of settling contained 760 ppm of carbon. After six days of settling, two samples contained 70 and 230 ppm of carbon. It is evident from these experiments that particles of graphite were readily dispersed in sodium, that some of these particles were small enough to pass through 5- μ -porosity filters, and that the degree of aggregation of the dispersion depended in some complex way on its previous history. Briefly, this study does not appear to support the existence of a readily measurable equilibrium in the graphite-

Table I-13

APPARENT CARBON CONTENTS OF SODIUM CONTAINED IN GRAPHITE CRUCIBLES

<u>Order of Sampling</u>	<u>Temp. (°C)</u>	<u>Carbon Content (ppm)</u>
1	158	88, 106, 55, 71, 72, 63 ^a
2	307	41, 56, 58, 57
3	455	101, 116, 108
4	291	61, 80, 47
5	157	74, 66, 130
<u>b</u>	375	59, 127, 96, 130, 45

^a Taken from Table I-12, Column 1.

^b A second master batch of sodium was used in this experiment.

sodium system, such as that reported by Gratton.¹⁶ Further work is required to clarify this situation.

d. Sodium-Gas Reactions

Impurities can be introduced into sodium by reactions with contaminants present in cover gases. Because such reactions are important with respect to sodium technology for nuclear reactors, the reactions of sodium with various gases are being investigated. Preliminary studies with dynamic and static systems have been made.

Helium containing 1000 to 2000 ppm each of oxygen, nitrogen, carbon dioxide, carbon monoxide, hydrogen, and methane was recirculated through liquid sodium in a stainless steel reactor. The sodium was supported on a stainless steel frit in order to disperse the gas and thereby assure good contact with the sodium. Experiments were conducted at 190, 300, 385, and 455°C. Samples of the gas phase were collected at intervals up to 6 hr and analyzed by mass spectrometry.

¹⁶ Gratton, J. G., KAPL-1807, June 30, 1957.

In all experiments, as was expected, oxygen and carbon dioxide were found to be consumed rapidly and completely within analytical limits of detection. Although the mass spectrometer did not distinguish between carbon monoxide and nitrogen because of their coincidence at mass 28, in all likelihood the carbon monoxide reacted completely while the nitrogen was unaffected. Hydrogen contents decreased to levels which were, presumably, in equilibrium with unsaturated solutions of hydrogen in sodium. Methane reacted rapidly at 455°C, but only negligible changes in its concentration were noted at lower temperatures.

After the reaction of methane with sodium at 455°C, purges at 300°C with either pure helium or helium containing about 1% hydrogen did not liberate methane from the sodium into the gas phase. These observations are not consistent with some recently reported experiments¹⁷ which were interpreted in terms of an equilibrium between gaseous methane and the carbon and hydrogen dissolved in sodium. Further studies will be made to determine if equilibrium can be established between methane in the cover gas and carbon in the sodium and, if such an equilibrium exists, whether the presence of sodium influences the equilibrium $C + 2H_2 \rightleftharpoons CH_4$.

Experiments with sodium in a static system were conducted at 150 to 350°C with carbon monoxide at pressures from 0.3 to 9 torr. The reaction kinetics appear to be very complex. The results so far indicate (1) an induction period or a minimum temperature for reaction; (2) a strong influence of sodium purity, (3) considerable variation of the kinetic order of reaction with respect to carbon monoxide, and (4) a small temperature coefficient of reaction.

F. Preparation of Fuels for Fast Reactors

1. Solid Refractory Fuels

Refractory compounds of uranium and plutonium, such as carbides, nitrides, and sulfides, show promise as reactor fuels capable of withstanding high temperatures and large burnups. Methods are being investigated for the preparation of these fuel materials, and the more promising methods are being used to provide sufficient quantities of these refractory fuels for fabricability evaluations and irradiation testing by the Metallurgy Division. During the past year, work has focussed on carbide and nitride preparations. The nitride preparations are discussed in the mobile blanket fuel section (I-F2). Studies of sulfide preparation have been summarized in a previous report (see ANL-6875, p. 76).

¹⁷ Johnson, D. L., Chromatographic Analysis of Gases Over Sodium, NAA-SR-8448, Sept. 15, 1964.

a. Preparation of Uranium Carbide by a Liquid-Metal Method

When degassed, activated charcoal is added to a zinc-magnesium solution of uranium at 800°C , uranium monocarbide (UC) is precipitated, and magnesium and zinc are removed from the carbide by siphoning and distillation steps. All the operations except the distillation step are done in the transfer furnace; Figure I-38 shows the equipment used in these operations. Both the retort and the transfer furnace are attached to a vacuum-helium glovebox, wherein all operations on the uranium monocarbide are performed. (A vacuum pump is used to remove the impurities from the glovebox by evacuation overnight; the box is filled with helium before operations are resumed during the day.) Because of the excellent pressing and sintering properties of UC prepared by this method, this process was scaled up to produce 0.5 to 1 kg of product per batch under controlled atmosphere conditions.

The current series of runs to produce uranium carbide for testing by the Metallurgy Division has been completed. Twelve runs were made using normal uranium and two runs using fully enriched uranium. Analytical and process data for the runs are given in Table I-14. Results of the fabrication and irradiation tests by the Metallurgy Division are not yet available.

The oxygen content of the product has been reduced below the limit (0.2 w/o oxygen) desired by the Metallurgy Division. Apparently reduction below 0.14 w/o (Run UC-10) cannot be achieved with the present degassing techniques. Heating activated charcoal to 850°C , with continuous evacuation, has produced a charcoal product containing about 2.0 w/o oxygen. (The activated charcoal contributes from 60 to 80 w/o of the final oxygen content

Figure I-38

EQUIPMENT FOR URANIUM MONOCARBIDE (UC) PREPARATION BY THE LIQUID-METAL METHOD

Table I-14

ANALYTICAL AND PROCESS DATA FOR URANIUM MONOCARBIDE (UC) PREPARED BY THE LIQUID-METAL METHOD

Run	UC-2	UC-3	UC-4	UC-5	UC-6	UC-7	UC-10	UC-11	UC-12	UC-13	UC-14
Scale (Uranium Charge), kg	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	0.5 ^c	0.5 ^c
Reaction Time, hr	8	8	8	8	8	12	8	8	12	12	19
Charge, C/U	1.20	1.20	1.20	1.10	1.10	1.10	1.02	0.90	1.02	1.02	1.02
Yield, g	393	233	474	398	332	407	343	444	714	388	471
Oxygen, w/o	0.39	0.60	0.61	0.29	0.30	0.20	0.14	0.29	0.18	0.24	0.56 ^a
Nitrogen, ppm	380	380	60	10	180	220	120	20	190	230	300
Total C, w/o	5.40	5.40	5.86	5.56	6.00	6.23	5.59	4.56 ^b	5.24	5.34	5.04
Uranium, w/o	92.0	90.0	92.5	93.8	90.5	90.6	90.4	94.2	93.0	94.2	92.9
Magnesium, w/o	0.19	1.02	0.20	0.15	0.20	0.26	0.12	0.01	0.08	0.07	0.11
Zinc, w/o	0.52	1.49	0.58	0.31	0.82	0.69	0.30	0.08	0.20	0.14	0.20
Species (X-ray)	UC	UC, UO ₂ Minor	UC	UC	UC	UC	α U, UC	UC	UC	UC	UC
Parameter, ^d A (X-ray)	4.959	4.959	4.959	4.959	4.959	4.960	4.959	4.960	4.960	4.960	4.960
Surface Area, m ² /g	2.73	1.86	1.49	0.28	3.75	0.96	0.58	Not Available	Not Available	Not Available	Not Available

^a Inadvertent exposure to a contaminated glovebox.^b Unreacted uranium left in product.^c 93 w/o ²³⁵U^d Lattice parameter of pure UC = 4.961 ^o Å.

Table I-15

PROCESS VARIABLES AND YIELDS FOR URANIUM MONOCARBIDE (UC) PREPARATION BY
LIQUID-METAL METHOD

Run	U Charge (g)	UC Yield (g)	U (by analysis) in UC (w/o)	Yield $\left(\frac{\text{U in UC}}{\text{U Charge}} \times 100 \right)$ (%)	Reaction Time (hr)	Settling Time (hr)	Type of Transfer Tube
UC-10	503	343	90.4	61.6	8	1	Straight
UC-12	1004	714	93.0	66.2	12	1.5	Straight
UC-13	470	388	94.2	77.8	12	1	Bent Upward toward Zn-Mg Melt
UC-14	524	471	92.9	83.5	19	3.75	Bent Upward toward Zn-Mg Melt

of the UC product.) Material with an oxygen content of 0.2 w/o or less can probably be produced consistently in future preparations.

The total carbon content of the UC products was generally higher than the maximum of 5.2 w/o desired by the Metallurgy Division and varied from 5.2 to 6.0 w/o. (The theoretical carbon content of UC is 4.8 w/o.) The C:U charge ratio has been progressively decreased from 1.20 to 1.02 in an attempt to decrease the total carbon content of the UC product, with no noticeable effect. However, in run UC-11 with a C:U charge ratio of 0.90, the carbon content of the product was 4.56 w/o.

The yield of UC product was increased from 61.6 to 83.5 percent over the last five runs (see Table I-15) by increasing the reaction and settling times and by changing the configuration of the transfer tube. The transfer tube was bent upward toward the Zn-Mg melt to minimize the entrainment of the settled UC particles during pressure siphoning.

Metallographic examinations of the UC products were made to determine the homogeneity of the UC particles. Typical particles are shown in Figure I-39. The individual particles were mounted, polished, and etched

Figure I-39

PHOTOMICROGRAPH OF TYPICAL URANIUM MONOCARBIDE PARTICLES

before viewing. In most cases, the particles exhibited two phases, a light shiny phase on the perimeter of the product and a gray phase in the center. Attempts are being made to identify these phases by electron probe analysis. The presence of two phases may significantly affect the preparation of a homogeneous fuel.

b. Preparation of Uranium Monocarbide by a Fluid-Bed Process

A study is being made of the conversion of powdered uranium metal to uranium monocarbide in a fluidized bed, using a mixture of propane and hydrogen as the reactant and fluidizing gases. The overall reaction is

This type of synthesis has been carried out in a static bed;¹⁸ however, under these conditions, the powdered uranium tends to sinter into a dense mass before conversion to the monocarbide is complete. The aim of the present studies is to produce a finely divided, free flowing product of stoichiometric composition, which can be pressed into a fuel without intermediate processing such as grinding and blending. Literature data¹⁹⁻²¹ indicate that the carbon content of UC can probably be controlled by the proper choice of the following variables: the hydrogen-hydrocarbon ratio, the reaction temperature, and the reaction time. Carbon deposition can be prevented at equilibrium conditions in a hydrogen-hydrocarbon gas mixture by proper adjustment of the H/C ratio.^{19, 21} In a fluid-bed, and at the proposed operating temperature of 600-700°C, equilibrium conditions probably are not established since the gases pass rapidly through the bed; however, the equilibrium data are useful as a guide in the choice of experimental conditions.

The fluid-bed reactor vessel is shown in Figure I-40. Reaction of uranium with the propane is carried out in the heated zone; a U-tube at the bottom of the vessel retains the powdered uranium in this zone. Above the reaction zone is a particle de-entrainment section containing a porous stainless steel filter. All operations, including loading and unloading of the vessel, are carried out in a helium atmosphere.

¹⁸ Accary, A., The Preparation and Fabrication of Uranium-Carbon Alloys, AERE-Trans 958 (1963).

¹⁹ Tevebaugh, A. D. and E. J. Cairns, Saturated Hydrocarbon Fuel Cell Program, ARPA, Order No. 24761, Dec. 31, 1962.

²⁰ Kalish, H. S. et al., The Development of UC as a Nuclear Fuel, NYO-2688, First Annual Report, May 1, 1959 to April 30, 1960.

²¹ Tevebaugh, A. D. and E. J. Cairns, CHO Gas Phase Composition in Equilibrium with Carbon, and Carbon Deposition Boundaries at One Atmosphere, J. Chem. Eng. Data, 9, 453 (1964).

Figure I-40

FLUID-BED REACTION VESSEL
FOR URANIUM MONOCARBIDE
PRODUCTION
(304 stainless steel)

The uranium charge material is prepared by first reacting uranium metal pins 3/8-in. in dia. with hydrogen at 250°C to produce UH_3 and then decomposing UH_3 at about 470°C. This procedure produces a finely divided uranium powder which has good fluidizing characteristics and can be readily reacted with propane.

In initial experiments, a gas velocity of 1.0 ft/sec was used to prevent possible sintering; however, this rate of flow resulted in considerable entrainment of uranium into the upper section of the reaction vessel. Most of the subsequent experiments have been carried out at gas velocities of 0.25 ft/sec without the occurrence of sintering.

A number of experiments have been carried out to produce UC on a 100 g scale. The effects of varying the time, temperature, and hydrogen-to-propane ratio have been studied. Experimental conditions and results of these runs are shown in Table I-16. X-ray diffraction analyses provided verification of the production of UC. Both hyper- and hypo-stoichiometric UC were produced by varying the

hydrogen-to-propane ratio. However, the precise conditions for producing stoichiometric UC have not yet been established. The oxygen content of recent experiments has varied from 0.55 to 1.0 w/o. In future work, an attempt will be made to reduce the oxygen content by having a purer atmosphere and by minimizing run time.

The particle sizes of both the UH_3 starting material and the UC product are shown in Table I-17. For these measurement it was necessary to use two special screens, one of 20- μ hole size and the other of 5- μ hole size. Five hours of fluidization at 700°C at a velocity of 0.25 ft/sec produced some decrease in particle size, but the increase of particles in the -5 μ range was small. The production of a large amount of fines (-5 μ) would be detrimental to the fluidizing characteristics of the bed since entrainment might occur or electrostatic attraction between very fine particles might cause agglomeration.

Table I-16

PRODUCTION OF UC BY THE FLUID-BED METHOD

Run No.	Time (hr)	Reactant Gases ^a		Analysis of Product		Phases Determined by X-ray Diffraction	
		H ₂	C ₃ H ₈	Total C	Oxygen	Major	Minor
		(v/o)	(v/o)	(w/o)	(w/o)		
Runs at 600°C							
UCF-4	5	10	90	6.5	2.2	UC	Possibly UC ₂
UCF-5	5.5	10	90	6.4	2.1	UC	Probably UC ₂
UCF-6	5.5	20	80	6.0	2.0	UC	Probably UC ₂ , Possibly UO ₂
UCF-7	5	70	30	5.3	0.90	UC	Probably UC ₂ , Possibly UO ₂
UCF-8	5	80	20	3.2	1.0	UC and βUH ₃	Possibly UO ₂ , Probably no UC ₂
UCF-17	5	75	25	3.8	1.2	UC	Possibly βUH ₃ , Possibly UO ₂
UCF-20	5	72	28	4.6	-	UC	βUH ₃ , Possibly UC ₂
Runs at 700°C							
UCF-9	3	80	20	5.4	0.70	βUH ₃ ^b	UC, Possibly UO ₂
UCF-16	5	90	10	3.4	0.50	UC	βUH ₃
UCF-19	5	85	15	4.8	-	UC	Possibly UC ₂ , Possibly βUH ₃
UCF-21	5	70	30	5.4	0.61	UC	Possibly UC ₂ and βUH ₃ (very minor)

^a Fluidizing gas velocity was 0.25 ft/sec except for Run UCF-4 in which it was 0.50 ft/sec.

^b Possible sample mix-up.

Table I-17

PARTICLE SIZE DISTRIBUTION OF UH_3 STARTING MATERIAL
AND UC PRODUCT FROM THE FLUID-BED PROCESS

<u>Particle Size (μ)</u>	<u>UH_3 (Batch 12) (w/o)</u>	<u>UC (Run UCF-19) (w/o)</u>
+74	0.0	0.0
-74 +44	0.8	0.3
-44 +20	75.5	11.5
-20 +5	23.4	87.2
-5	<u>0.3</u>	<u>1.2</u>
	100.0	100.2

Since this method shows significant promise of producing UC material suitable for use as reactor fuel, additional work is underway. Length of reaction time, higher temperatures, and the hydrogen-propane composition region where free carbon deposition can be prevented will be investigated; efforts will also be made to reduce the oxygen content of the product.

c. Homogeneous Precipitation of Plutonium-Uranium Carbides from Fused Salts

A search for better methods of preparing actinide carbide fuels revealed that magnesium sesquicarbide (Mg_2C_3) reacts with UF_4 or UCl_3 in a molten salt mixture (35 m/o LiCl -65 m/o MgCl_2) to precipitate uranium monocarbide from solution. The primary interest in a homogeneous precipitation reaction was its possible use for the preparation of a uranium-plutonium monocarbide solid solution. Initial experiments with plutonium showed that the reaction of PuCl_3 with Mg_2C_3 in the molten salt mixture produced Pu_2C_3 rather than the desired monocarbide (see ANL-6875, p. 75). Nevertheless, the method appeared worthy of further study to determine if simultaneous precipitation of the uranium and plutonium carbides would yield the desired solid solution, $(\text{U}_x\text{Pu}_{1-x})\text{C}$.

The experimental procedure consisted basically of: (1) reacting PuCl_3 and UCl_3 with Mg_2C_3 in the molten salt mixture for 1 hr. at 625-650°C, and (2) recovering the carbide product by volatilization of the salt phase under vacuum at 850°C. Because of plutonium toxicity, all experiments were carried out in gloveboxes. A one module box with a purified helium atmosphere was

Table I-18

SUMMARY OF PLUTONIUM-URANIUM CARBIDE PRECIPITATION EXPERIMENTS

Conditions: ratio of 4 UCl_3 : PuCl_3 (approx. 10 g U)
heated in molten salt at 650°C for 1 hr.

Experiment No.	Molten Salt	Yield (%)	Composition of Precipitated Product (w/o)						Phases shown by X-Ray Diffraction ^c	
			Uranium	Plutonium	Carbon	Oxygen	Insoluble ^a	Free Carbon ^b	Major	Minor
1	35 m/o LiCl-65 m/o MgCl_2	72	84.5	6.4	4.12	1.34	~3.	~2.	FCC 4.96	
2	35 m/o LiCl-65 m/o MgCl_2	70	89.0	3.3	4.46	1.0	1.1	0.9	FCC 4.959	
3	35 m/o LiCl-65 m/o MgCl_2	87	67.6	11.5	7.69	0.94	6.7	4.8	FCC 5.47 FCC 4.96	
4	LiCl	-	38.4	10.2	^d	^d	1.2	1.0	FCC 4.96 BCC 8.09	
5	LiCl	-	63.9	12.1	5.81	2.20	~10.	1.2	FCC 4.959	BCC 8.13

^a Material insoluble in ~12M HNO_3 .

^b Material insoluble in HNO_3 , subsequently volatilized at 1000°C.

^c Lattice parameters of pertinent phases are: UO_2 , 5.468; PuO_2 , 5.396; PuO , 4.96; PuC , 4.959-4.973; UC , 4.961; U_2C_3 , 8.088; Pu_2C_3 , 8.129.

^d Not determined.

used to handle all materials and to load and unload the reaction vessels. This box was connected by means of a vacuum lock to a larger box with a nitrogen atmosphere in which the furnace was located. During routine operation, the helium atmosphere box contained 12-20 ppm moisture.

The data from five precipitation experiments are given in Table I-18. The overall yield of carbide product, based on the original weight of uranium and plutonium, varied from 70 to 88 w/o for the three experiments for which weight data are available. Precipitation from the salt phase was determined to be complete. However, the salt phase, condensed after the volatilization step, contained substantial amounts of plutonium (20-50 w/o of the original plutonium). This was probably a result of reaction between the precipitated plutonium carbide and the magnesium chloride of the molten salt. An attempt to minimize this effect by using only lithium chloride as the salt phase was only partially successful. The product was also contaminated with free carbon and oxygen.

For the first two experiments (see Table I-18), X-ray diffraction results indicated that the dominant phase had a face-centered cubic crystal symmetry and a lattice parameter of $4.960\text{\AA}$. This is the lattice parameter for UC and is the value to be expected for solid solutions of (U-Pu)C up to approximately 15 to 20 a/o plutonium.

In later experiments, X-ray results revealed the presence of substances with body-centered cubic symmetry and lattice parameters of $8.09\text{\AA}$ and $8.13\text{\AA}$. These values are the lattice parameters of U_2C_3 and Pu_2C_3 , respectively. In these experiments, the plutonium content of the precipitate was higher than in the first two experiments. The appearance of sesquicarbide phases in products with higher plutonium compositions suggests that sesquicarbide might have been present in the first two preparations, but was undetected by X-ray diffraction techniques. It is difficult to conclude from these experiments that a true solid solution of UC-PuC had been formed.

Further work on the homogeneous precipitation method for the preparation of uranium and plutonium monocarbide is not planned for the following reasons:

1. Pu_2C_3 is apparently formed instead of or in addition to the desired solid solution of (U-Pu)C.
2. Large amounts of free carbon were found in the carbide products and the bound carbon contents were variable.
3. Magnesium sesquicarbide was difficult to prepare in pure form and the yields were low (40-50%). The use of other metal carbides such as lithium carbide or sodium carbide may have been a better choice than Mg_2C_3 , but experiments with these carbides are not presently contemplated.

2. Studies of Mobile Blanket Fuels for Fast Reactors

Mobile blanket fuels for fast breeder reactors show promise of reducing reactor down-time for fuel shuffling, improving sodium coolant utilization and, thus, power conversion efficiency, and decreasing fuel processing and refabrication costs. Experimental work has been initiated to develop a paste blanket fuel consisting of a ceramic fuel dispersed in a liquid metal. Currently, the most attractive of the mobile blanket fuels which have been considered is a paste of uranium mononitride (UN) in sodium.

a. Reactor Requirements for Mobile Fuel Blankets

If reactors with mobile fuel blankets are to have an economic advantage over reactors with solid fuel blankets, the advantages must be gained without great changes in the core design. The nuclear characteristics of the core, the ease of removal of the core fuel, and the core fuel cycle costs have much greater effects on the overall economics of the reactor than do blanket characteristics. Since core characteristics are optimized for minimum power costs consistent with safety, gross changes in the core to accommodate a mobile blanket would negate the economic advantages of a mobile blanket fuel. Accordingly, it is believed that a mobile fuel would not be suitable for axial blankets since removal of the core fuel would be complicated by such blankets, particularly the top blanket. Mobile blanket fuel appears to be best suited for reactors requiring large radial blankets and producing a high fraction of the breeding in the radial blanket.

b. Property Requirements of Paste Blanket Fuels

The nuclear requirements for blanket fuels are less stringent than for core fuels because most of the nuclear interactions, particularly the fissions, take place in the core. Thus, degradation of the neutron energy spectrum in the blanket by the addition of moderators has only a slight effect on the overall breeding ratio. However, a high uranium density in the blanket fuel can be beneficial in providing high neutron capture efficiency for a relatively thin blanket. For this reason, pastes with liquid-metal vehicles containing at least 50 v/o solid fertile material appear to be more attractive blanket fuels than dilute slurries or molten uranium salt solutions.

The shift of a given amount of fuel in the blanket has a smaller effect on reactor reactivity than a shift of the same amount in the core. However, even in the blanket, shifts in uranium density are undesirable. This consideration again favors low-mobility settled pastes which would appear to be more stable than slurries, since the latter depend on fluid motion to maintain an even distribution of solid particles.

Although a static paste fuel contained in sealed tubes in much the same way as solid fuel might be feasible, the present experimental effort is

being directed toward developing a paste fuel which could be circulated. The advantages of a circulating paste fuel are as follows:

1. Fission product gases can be continuously separated from the fuel by circulating the fuel through a separating device.
2. Fuel in a circulating blanket system may be frequently or even continuously removed for reprocessing without reactor shut-down.
3. The build-up of plutonium to high concentrations in the region of the core and the associated heat removal problem which is common to reactors with stationary fuel may be avoided by circulation of the fuel.

These advantages can be gained by having a flow velocity of only a few feet per hour, a velocity that is easily obtainable with a heavy paste. Good paste flow characteristics may require finely ground solid particles with a narrow size range. In order to maintain these flow characteristics, the particles must be nonsinterable under reactor conditions. Low solubility of the solid particles in the liquid metal vehicle is also a necessity, since mass transfer effects, i.e., growth of the particles and deposition of material, might result in stopping of the flow of blanket paste. Another phenomenon which would stop paste flow and also result in overheating of the fuel would be sudden de-wetting of the solid particles by the liquid metal. This might result from (1) a gradual change in the composition of the solid or liquid phases of the paste, or (2) gas evolution from the solid.

It would be impractical to remove the heat developed in paste blanket fuel by circulating it to an external heat exchanger because the pumping rate required would be too high for a viscous paste. Therefore, it would be necessary to contain paste blanket fuel in tubes and to remove the heat by a coolant such as sodium, as is done in solid-fueled fast reactors. The rate of heat removal (which equals heat generation at equilibrium) from a paste contained in a tube is given by the following relationship for heat transfer from a rod with uniform internal heat generation:

$$q = \frac{4 k \Delta T}{r^2}$$

where q = heat generation rate per unit volume,

k = thermal conductivity of fuel,

ΔT = temperature differential between the center line and the periphery of the fuel rod, and

r = radius of fuel rod.

It is apparent that the boiling point of the vehicle of paste fuels, which controls the maximum allowable center-line temperature, and the thermal conductivity of the fuel are important fuel characteristics. A sodium-vehicle paste would require a center-line temperature limitation set safely below the 1621°C boiling

point of the sodium vehicle. Alloy vehicles with a lead or bismuth base would have an advantage over sodium since they have higher boiling points. However, this advantage would be partially offset by the relatively low thermal conductivity of bismuth, lead, and their alloys.

Compatibility of the fuel with the container material is a stringent requirement because the expensive circulating system must endure for five to ten years to be economical. It would seem easier to meet this goal with a sodium vehicle than with a vehicle of bismuth or lead alloys which are more corrosive than sodium to stainless steel, the probable container material. It is also possible that tubing containing the paste would be attacked by decomposition products from a ceramic fertile material constituting the solid phase of a blanket paste. In uranium carbide-sodium pastes, carbon which is transferred from hyperstoichiometric UC through sodium may cause failure of the tubing by carburization.²² In uranium dioxide-sodium pastes, sodium may reduce the oxides of fission products²³ to form sodium oxide which would render the sodium more corrosive to stainless steel tubing.²⁴ Since UN is compatible with sodium²⁵ and stainless steel,²⁶ it appears that a paste of UN in sodium would be innocuous for use with stainless steel.

In summary, the following characteristics are desirable for the components and the paste fuel to be used in the blanket of a fast reactor:

A. Fertile Particle Characteristics

1. Nonsinterability
2. Low solubility in vehicle
3. Chemical stability relative to vehicle, fission products, and container
4. High bulk density
5. Fine, uniform particle size
6. High thermal conductivity

B. Vehicle Characteristics

1. Noncorrosiveness
2. High thermal conductivity
3. High boiling point

²² Webb, B. A., NAA-SR-6246, May 1963.

²³ Epstein, L. F. and J. Nigriny, AECD-3709, 1948.

²⁴ Brush, E. G., Corrosion, 11, p. 229t (1955).

²⁵ Wullaert, R. A. et al., BMI-1638, June 1963.

²⁶ Katz, S., J. Nucl. Mater. 6, 172 (1963).

C. Paste Characteristics

1. Stable wetting of particles by vehicle
2. Uniform high uranium density
3. Compatibility with container
4. Stable fluidity
5. High thermal conductivity

A paste consisting of UN suspended in sodium appears to fulfill many of the requirements listed above better than the other pastes considered. Experiments are underway to prepare and test the selected paste to determine whether it can meet the exacting requirements of paste blanket fuel.

c. Preparation of Uranium Mononitride

Uranium mononitride powder was prepared by reaction of nitrogen with uranium shot at 800 to 1350°C and subsequent grinding of the product. The method developed in this work produces UN powder of unusually high bulk density.

Several methods for preparing UN are described by Katz and Rabinowitch.²⁷ The standard procedure is first to prepare mixed crystals of U_2N_3 and UN_2 by a method similar to the following:

- (1) Direct reaction of uranium with nitrogen at 800 to 1000°C.
- (2) Reaction of UH_3 with nitrogen at 250 to 350°C.
- (3) Reaction of UH_3 with NH_3 at 200°C.

The product of these preparations is then decomposed to UN and nitrogen by heating to 1300°C or higher under reduced pressure. These methods yield products with bulk densities of 3 to 7 g/cc.

The object of the present work was to shorten the time of preparation by carrying out the reaction at a temperature high enough to avoid formation of the higher nitrides. In addition, such a preparation might yield a product of high bulk density. Uranium, in the form of shot or turnings, was nitrided at 200 to 400 torr pressure. The temperature was maintained at 900 to 1050°C for several hours. Before a nitrogen-to-uranium ratio of one was reached, the temperature was gradually increased to about 1300 to 1350°C. The higher temperature was maintained until nitriding was complete.

In an experiment with 90 g of uranium turnings, 40% of the nitrogen reacted at temperatures above 1100°C. The reaction stopped after 20 min at the final reaction temperature of 1300°C. (The nitride coating on the turnings

²⁷ Katz, J. J. and E. Rabinowitch, The Chemistry of Uranium, Doven Publications, Inc., New York, 1951.

contained the molten uranium, m.p. 1132°C , during the last step of this process.) The pressure was reduced to 5×10^{-5} torr in a period of 15 min with no evidence of nitrogen evolution from the reaction product. The product was dark gray and in the form of the original turnings. It was easily ground into a coarse (~ 100 -mesh) powder having a bulk density of 8.0 g/cc, which is higher than is usually obtained for uncompacted UN powder. X-ray analysis of a sample of -400 mesh powder indicated a major phase of UN with a minor phase of the U_2N_3 of hexagonal structure²⁸ and a lesser amount of UO_2 . The lattice constant for the UN phase was $4.890 \text{ \AA}$, which is in good agreement with a recent literature value.²⁹ Analysis of the product for nitrogen by combustion to U_3O_8 and correction for the oxygen content (0.095%) of the sample yielded a nitrogen content of 5.60%. (The nitrogen content of stoichiometric UN is 5.557%.)

In a second UN preparation by this general procedure, the reaction terminated before the temperature reached 1300°C . Nitrogen was evolved as the pressure was reduced, thereby indicating that higher nitrides had formed during nitridation. The bulk density of the powdered product, 6.1 g/cc, was considerably less than the value of 8.0 g/cc obtained in the first run (in which less of the higher nitrides were formed).

In later experiments with charges of one kilogram of uranium shot (0.71 to 1.41 mm in dia.) a product was obtained with similar characteristics to that obtained with turnings. However, it was necessary to do the initial heating of the dense charge of shot under a nitrogen atmosphere to prevent sintering of the particles before the initial operating temperature of 800 to 900°C was reached. The UN product ground for 24 hr to about 325 mesh median size is suitable for making UN-sodium paste of 50 v/o solids content.

d. Preparation of Uranium Mononitride - Sodium Paste

After the preparation of a suitable uranium mononitride powder was achieved, direct preparation of a paste was undertaken. In initial experiments, UN powder was heated with sodium at various temperatures in an alumina crucible. Wetting of the UN by sodium was clearly achieved at 300 to 500°C after 1/2 hr of stirring; at 250°C , 1 hr of stirring was required. No instances of dewetting of the UN on cooling were observed in any of these experiments.

Following this preliminary work, preparation of a UN-sodium paste of high uranium content was attempted. The UN powder ($\sim 100\mu$ median dia.) with a bulk density of 8.2 g/cc was mixed with sodium at 300°C to obtain 346 g of paste containing 49 v/o solids (6.6 g/cc uranium). The paste appeared to

²⁸ Vaughan, D. A., X-ray Diffraction Study of the Nitrides of Uranium, J Metals 8, AIME Trans. 206, 78, (1956).

²⁹ Evans, P. E., T. J. Davies, Uranium Nitrides, J. Nucl. Mater. 10 (1), 43 (1963).

contain 8 v/o gas, as determined by difference from the amounts of sodium and UN added.

At 40 v/o solids, an intermediate stage in the preparation, the paste was judged to have good flow properties. However, in its final composition (49 v/o solids) the paste was quite viscous and probably not directly suitable for a flowing system. Additional experimentation is underway to obtain a paste of high uranium density, low gas content, and good flow properties.

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

Reprocessing of irradiated fuels has been accomplished successfully for many years by solvent extraction processes. These reprocessing methods, however, may not be so well suited to very high burnup, privately owned fuels from future commercial power reactors. Considerable interest, therefore, has developed in fluoride volatility reprocessing methods, in which the reagents employed are not sensitive to intense radiation. In particular, the ANL fluidized-bed fluoride volatility process has attracted considerable attention because it appears to have flexibility for application to a variety of fuels, both those containing fully enriched uranium-235 and those containing slightly enriched uranium. After irradiation, the latter fuels contain plutonium, which must also be recovered.

A cooperative program to promote the development of a single, fluidized-bed process is being undertaken by groups at four AEC laboratories. In addition to Argonne, these laboratories include Brookhaven National Laboratory, Oak Ridge National Laboratory and the Oak Ridge Gaseous Diffusion Plant. Responsibility for the design of a "hot" pilot plant to investigate the reprocessing of irradiated fuels has been undertaken jointly by the two groups at Oak Ridge.

The high level of interest in the process development program is exemplified by a large number of visits to the ANL Chemical Engineering Division by industrial firms seeking technical information. In addition, public announcements have been made by at least one industrial concern of plans to exploit fluoride volatility techniques in a full-scale reprocessing plant.

To aid in coordination of the development program, a reference flow-sheet for reprocessing Zircaloy-clad, slightly enriched UO_2 fuel has been selected (Figure II-1). This flowsheet is not considered optimum, but is based on techniques for which the most knowledge is available. It involves the following steps: (1) removal of the Zircaloy cladding by reacting it with gaseous hydrogen chloride to form volatile zirconium tetrachloride (ZrCl_4), (2) conversion of ZrCl_4 to the solid oxide in a second vessel by reaction with steam (pyrohydrolysis), (3) fluorination of the uranium and plutonium oxides to the hexafluorides, UF_6 and PuF_6 , (4) separation of the PuF_6 from UF_6 by thermal decomposition of PuF_6 to solid plutonium tetrafluoride (PuF_4), and (5) decontamination of the UF_6 by fractional distillation, aided by solid adsorption techniques.

A number of alternative flowsheets are under investigation which are intended (1) to improve and simplify the reference flowsheet, and (2) to provide flexibility for the processing of other fuels such as stainless steel-clad

Figure II-1

FLUID-BED FLUORIDE VOLATILITY PROCESS

UO_2 . It is believed that a plant designed to process low enriched fuels could, with some equipment additions, also process high enrichment fuels.

A. Laboratory Studies

Laboratory studies were continued in support of the program for the development of the fluoride volatility process for the recovery and purification of nuclear reactor fuels. The major effort during the past reporting period concerned the development of techniques for the removal of plutonium from the inert solid, alumina, which is used as the fluidized medium in fluid-bed reactors. During this period, information was also obtained on certain aspects of the chemistry of plutonium hexafluoride and selected fission products, on the fluorination of plutonium in solid waste materials, and on the location of plutonium on alumina grains.

In the fluoride volatility process, spent reactor fuel is charged into a reactor containing granular, fired alumina. The alumina is heated and fluidized by a stream of nitrogen. Addition of a gaseous reagent such as hydrogen chloride or mixtures of hydrogen fluoride (HF) and oxygen (O_2) to the fluidizing gas effects the removal of the metallic cladding surrounding the oxide fuel. Hydrogen chloride is used to react Zircaloy cladding, and HF- O_2 is used for stainless steel cladding. Following the decladding step,

the fuel in the fluidized bed is treated with elemental fluorine to convert uranium and plutonium to the hexafluorides which volatilize from the heated reactor. Subsequent condensation, separation and purification steps applied to the hexafluorides result in isolation of decontaminated uranium and plutonium.

A previous report (ANL-6875, pp. 97-107) presented the results of several types of experiments which were designed to optimize the removal of plutonium from the inert solid (Al_2O_3) used as bed material in fluid-bed reactors. Briefly, the results indicated the following:

(1) Experiments in which powdered mixtures of U_3O_8 , PuO_2 , and fission product oxides were fed pneumatically into a heated, fluidized bed of alumina and contacted with dilute, elemental fluorine at 500°C resulted in the volatilization, as hexafluorides, of most ($>99\%$) of the uranium but not all (70-95%) of the plutonium. When the bed was then contacted with 100% fluorine at 500 or 550°C for 5-15 hr, little more plutonium volatilized. The presence of fission products in the original mixture proved detrimental to the removal of plutonium from the bed.

(2) Experiments in which samples of U_3O_8 , PuO_2 , and fission product oxides were first fed pneumatically into a heated, fluidized bed of Al_2O_3 , contacted with dilute fluorine at 450°C , and finally subjected to fluorination by 100% fluorine at 450°C for 5 hr, 500°C for 5 hr, and 550°C for 10 hr resulted in the removal of essentially all of the uranium ($>99\%$) and a large fraction (96-99%) of the plutonium. These data indicated that the gradual increase in temperature during fluorination using 100% fluorine appeared to increase the removal of plutonium.

(3) Experiments in which only PuO_2 or PuO_2 mixed with fission product oxides were fed to a heated, fluidized bed of alumina, fluorinated at 500°C by dilute fluorine and finally reacted with 100% fluorine at 550°C for 10 hr resulted in removal of a large fraction (96-98%) of the plutonium. The extent of removal of plutonium from the bed appeared to be dependent on the presence or absence of fission products.

(4) Experiments were carried out in which successive batches of U_3O_8 - PuO_2 -fission product oxides were fed pneumatically to a heated, fluidized bed of alumina and reacted with dilute fluorine at 500°C . Since the reaction of dilute fluorine served mainly to remove uranium, the accumulated plutonium was treated with 100% fluorine at 500 or 550°C for 10 hr, but incomplete plutonium removal (85%) was observed.

These results indicated that adequate removal of plutonium would be obtained only when the bed material was subjected to relatively severe fluorination conditions. The results also indicated that introducing the powdered sample while the fluid bed was at a lower temperature (for example, 450°C

instead of 500°C) resulted in a greater ultimate plutonium removal when the bed was later fluorinated at elevated temperatures (500, 550°C). These conclusions formed the basis of selection of conditions for experiments to be reported at this time.

1. Recovery of Plutonium from Alumina Bed Materials

a. Reuse of Al_2O_3

On the basis of past experimental results, the fluorination of plutonium from a fluidized bed of Al_2O_3 to relatively low levels of residual plutonium can be accomplished by treatment of the bed material with 100% fluorine at elevated temperatures. Since the initial quantity of plutonium charged is small, however, it is likely that extensive reaction times would be required to reduce the residual plutonium to the desired level of less than 1% of the plutonium initially charged to the reactor. In order to avoid excessive reaction time while at the same time maintaining a high degree of removal of plutonium from the bed, the quantity of plutonium charged to the bed should be increased by reusing the bed for the fluorination of several batches of plutonium-uranium oxide mixtures. It has already been shown that, unless plutonium is removed from the bed to a significant degree after each addition, the residual plutonium content after multiple additions is too high for process consideration. Hence, a series of experiments was performed in which multiple additions of U_3O_8 - PuO_2 - F.P. (fission product) mixtures were made to the bed, and following each addition, the bed contents were contacted with 100% fluorine for 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C. The results, shown in Table II-1, part A, indicate that if the procedure outlined above is employed, multiple reuse of the Al_2O_3 bed results in removal of plutonium to levels acceptable for process use. The low removal of plutonium after the third addition of feed to the bed is believed to have been due to operational difficulties with the equipment during that test. It can be seen that further additions of feed and subsequent fluorinations of the bed negated the poor results obtained in the third addition. Further, although the last addition (Cycle 8) employed a larger concentration of plutonium (3 w/o) than had been used in the first seven additions (0.4 w/o), satisfactory removal of plutonium was obtained.

The experiments listed in part A of Table II-1 used a mixture of fission products from which molybdenum had been omitted. This was done because previous experience had shown (ANL-6900, p. 150) that the presence of molybdenum usually caused operational difficulties associated with plugging of lines and valves by a slightly volatile molybdenum fluoride such as MoO_2F_2 or MoF_5 (see Behavior of Molybdenum in HF-O_2 and in Fluorine later in this section). A set of experiments was carried out in which molybdenum was added (22 w/o of the fission product oxides) to the fission product mixture in the feed. The results of this series of experiments, performed in the same manner as the series which did not include molybdenum, are tabulated in

Table II-1

FLUID-BED FLUORINATION OF U_3O_8 - PuO_2 -FISSION PRODUCT MIXTURES:
EFFECT OF REUSE OF ALUMINA FOR SEVERAL ADDITIONS AND
FLUORINATIONS ON PLUTONIUM RETENTION OF ALUMINA

Feeding-Fluorination Period

Temperature:	450°C
Total Gas Flow Rate:	12 liters/min (1.6 ft/sec at 500°C)
Fluorine Concentration in Total Flow:	20 v/o
Alumina in Bed:	400 g (120 mesh)
Alumina in Feed Materials:	150 g (+20 g wash, 120 mesh) ^a

Recycle-Fluorination Periods

Temperature, Time:	450°C, 5 hr; 500°C, 5 hr; 550°C, 10 hr
Total Gas Flow Rate:	8 liters/min (1.2 ft/sec at 500°C)
Fluorine Concentration:	100%

Addition- Fluorination Cycle	Feed Material ^b			Feed Rate (g U ₃ O ₈ -PuO ₂ per min)	Retained on Alumina Bed				% of Total Pu Volat- ilized ^c
	Pu (g)	U (g)	F.P. (g)		Pu (w/o)	Pu (g)	U (w/o)	U (g)	
A. Experiments in which the fission product mixture did not contain MoO ₃ ^d									
1	0.986 (0.986) ^e	250	1.99	1.6	0.0046	0.026	0.010	0.057	97.4
2	1.182 (2.168)	254	2.56	3.3	0.0036	0.021	0.009	0.051	99.0
3	1.182 (3.350)	254	2.56	2.2	0.193	1.175	3.60	21.92	65.0
4	1.162 (4.512)	248	2.54	1.8	0.012	0.070	0.042	0.245	98.4
5	1.198 (5.710)	254	2.60	2.2	0.010	0.058	0.039	0.226	99.0
6	1.194 (6.904)	254	2.60	1.5	0.0093	0.054	0.025	0.145	99.2
7	1.223 (8.127)	256	2.60	1.5	0.0088	0.051	0.043	0.250	99.4
8	8.647 (16.774)	234	16.00	1.1	0.025	0.150	0.004	0.024	99.2
B. Experiments in which the fission product mixture contained MoO ₃ ^f									
1	0.990 (0.990) ^e	254	2.58	2.22	0.003	0.017	0.009	0.052	98.3
2	1.209 (2.199)	254	2.58	2.27	0.030	0.171	0.006	0.034	92.2
3	1.213 (3.412)	254	2.58	2.25	0.028	0.161	0.105	0.604	95.3
4	1.225 (4.637)	257	2.62	2.30	0.018	0.105	0.070	0.403	97.7
5	1.218 (5.855)	254	2.58	2.50	0.014	0.082	0.005	0.028	98.6

^a 20 g Al_2O_3 were passed through the feed apparatus to wash out the apparatus and assure transfer of all plutonium-containing solids.

^b Composed of about 300 g of a U_3O_8 - PuO_2 -fission product mixture containing about 0.4 w/o Pu, 84 w/o U, and 0.85 w/o F.P. oxides (for the quantity of the individual oxides in the fission product oxide mixture, see ANL-6800, p. 201, Table II-1) mixed with 150 g of nominal 120 mesh alumina.

^c Based on the quantity of plutonium retained in the alumina bed and that fed to the fluid-bed reactor.

^d The fission product mixture contained the following oxides: La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Y_2O_3 , BaO , and ZrO_2 .

^e Figures in parentheses are the cumulative quantities of plutonium fed to the fluid-bed reactor.

^f The fission product mixture contained those oxides listed in footnote d plus 22 w/o MoO_3 .

part B of Table II-1. Although an increase in the plutonium concentration remaining in the bed is observed when these results are compared to those shown in part A of Table II-1, it should be pointed out that if the final plutonium concentration observed after five additions (0.014 w/o) had been maintained for two further additions of feed containing 0.4 w/o plutonium, the cumulative removal of plutonium would have been greater than 99% at the end of the seventh addition experiment. The results obtained from experiments which included molybdenum indicate that although the presence of molybdenum affects the course of plutonium removal during fluorination of successive batches of feed, satisfactory recovery of plutonium may still be achieved. However, the contribution of equipment factors to the retention of plutonium cannot be dismissed.

b. Location of Plutonium on Al_2O_3 Particles

A study of the location of plutonium on the alumina grains was made to define whether the plutonium is retained on the surface or dispersed throughout the grains, since the location could influence the choice of chemical treatment required to remove the plutonium from the grains. Owing to the low residual concentration of plutonium in alumina, the identity of the plutonium compounds in the bed was not determined. It was possible, however, to show that the plutonium is retained on the surface and not in the interior of the alumina grain. Figure II-2 is a micrograph of an autoradiograph of sectioned grains of alumina obtained from a bed after fluorination. The plutonium concentration in the bed was 0.12 w/o.

Figure II-2

MICROGRAPH OF AUTORADIOGRAPHIC EMULSION, FIVE-HOUR EXPOSURE AR-10 AUTORADIOGRAPHIC EMULSION, SHOWING ALPHA TRACKS DUE TO PLUTONIUM ON SURFACE OF FLUID-BED ALUMINA

The dark outlines shown in Figure II-2 are due to alpha tracks and mark the shape of the alumina grains; individual alpha tracks can be seen at the edges of the darkened area. This micrograph shows clearly that the plutonium is located only on the surface of the alumina grains, and this material should be more readily removed during fluorination than plutonium present in the interior of the grains.

c. Plutonium Content of Alumina Bed Material After Blank Runs

The retention of plutonium in the alumina bed after fluorination of a plutonium-containing bed has been as low as 0.002 w/o in experiments in which only plutonium and fission

products were charged to the reactor (see ANL-6875, pp. 98-101). It is generally observed, however, that all surfaces of the equipment are contaminated by plutonium. The magnitude of this contamination and its effect on the observed residual plutonium detected in bed material are of interest. A series of four experiments was performed to determine the residual plutonium content of a bed which had been subjected to the treatment of a typical experiment but to which no plutonium had been added. Table II-2 lists the results obtained in four of the "blank" experiments. Prior to experiment 2, a new manifold, new traps and a new disengaging chamber filter were installed after a test involving the processing of feed material with a normal (low) level of plutonium.

Table II-2

FLUID-BED FLUORINATION OF OXIDE FUELS: DETERMINATION OF
RESIDUAL PLUTONIUM CONTENT IN BLANK EXPERIMENTS

Feeding-Fluorination Period

Temperature: 500°C
Total Gas Flow Rate: 12 liters/min
Fluorine Concentration in Total Gas Flow: 20 v/o

Alumina in Bed: 400 g

Alumina in Feed: 170 g

Recycle-Fluorination Period

Temperature: 550°C
Time: 10 hr
Total Gas Flow Rate: 8 liters/min
Fluorine Concentration: 100%

Experiment	<u>Feed Material</u>		<u>Analytical Results</u>			
			<u>Alumina Bed</u>		<u>Disengaging Chamber</u>	
	<u>wt Pu (g)</u>	<u>wt F.P. (g)</u>	<u>Pu (w/o)</u>	<u>Pu (g)</u>	<u>Pu (w/o)</u>	<u>Pu (g)</u>
1	None	19.4 ^a	0.0045	0.028	0.32	0.060
2	None	None	0.0007	0.004	0.50	0.006
3	None	None	0.0015	0.011	0.32	0.006
4	None	14.9 ^a	0.0055	0.033	0.235	0.017

^a The F. P. mixture contained the following: La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Y₂O₃, BaO, ZrO₂, and MoO₃. For relative concentrations of the fission product oxides, see ANL-6800, Table II-1, p. 201.

The observed plutonium concentration (0.0007 w/o) found in the alumina bed in this experiment can be considered as the lowest plutonium concentration likely to be observed in the 1 1/2 in. fluid-bed system. Experiment 3 was performed following an experiment in which a normal level of plutonium was used as feed. Experiments 1 and 4 followed fluorination experiments in which high levels of plutonium were used as feed. On the basis of the results of these blank experiments, it appears that an average value of 0.003 w/o plutonium in alumina represents the background level of plutonium in the apparatus. Consequently, determination of the removal of plutonium from the alumina bed becomes uncertain when only low residual plutonium contents are found in the alumina bed. This, in turn, implies that more than 1.70 g plutonium must be contained in the feed in order to attach significance to a plutonium retention level of 1%.

The retention of plutonium on the filter located in the disengaging chamber may also be significant in the determination of minimum residual plutonium in the reaction system. Examination of a set of filters after 26 experiments indicated that approximately 3.5 μ g plutonium was retained in the filter per square inch of filter surface and per gram of PuF_6 passing through the filter.

d. Effect of Fluorine Flow Rate On Removal of Plutonium

The need for excessive quantities of fluorine to effect the removal of plutonium is avoided in the present experiments by recycling the reagent gas through cold traps to condense PuF_6 , followed by compression of fluorine by a Lapp Pulsafeeder in order to reintroduce the gas into the fluid-bed reactor. It would be desirable, from the standpoint of the chemistry of the process step, to permit considerable flexibility in the operational parameters of the fluid bed. Several experiments were performed to determine the effect of fluorine flow rate on the removal of plutonium from the alumina bed material.

In these experiments, the feed material was mixed with the appropriate amount of alumina and the total charge was placed in the reactor prior to the start of the experiments. This procedure is in contrast to that used in experiments reported elsewhere, wherein the feed was gradually transferred into the heated, fluidized bed in a stream of gas. The conditions employed and the results obtained from the present experiments are shown in Table II-3. The results indicate that a low flow rate of fluorine reduces the rate of removal of plutonium and results in inadequate plutonium removal during a fixed reaction time. It should be pointed out, however, that the fractional degree of removal of plutonium from the alumina bed is dependent on the amount of plutonium introduced as well as the amount of plutonium retained on the bed.

Several experiments were carried out using a static bed of alumina

Table II-3

FLUID-BED FLUORINATION OF PuO_2 -FISSION PRODUCT MIXTURES:
EFFECT OF FLUORINE FLOW RATE ON PLUTONIUM RETENTION
ON ALUMINA BED

<u>Solid Charge to Reactor:</u>	1.4 g PuO_2 (1.25 g Pu) 2.0 g Fission Product V Mixture ^a 570 g 60 mesh Alumina (+170) ^b
<u>Gas Phase:</u>	100% Fluorine
<u>Recycle-Fluorination Periods:</u>	450°C, 5 hr; 500°C, 5 hr; 550°C, 10 hr

Fluorine Flow Rate (liters/min) ^c	Linear Velocity (ft/sec) ^d	<u>Alumina Bed Analysis</u>		% of Pu Volatilized
		<u>Pu (w/o)</u>	<u>Pu (g)</u>	
4	0.43	0.026	0.148	88.2
4	0.43	0.019	0.108	91.4
6	0.66	0.0038	0.022	98.2
7	0.77	0.0038	0.022	98.2
8	0.87	0.0022	0.013	99.0
8 ^e	0.87	0.0022	0.013	98.0

^a Fission Product V mixture contains the following oxides: La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Y_2O_3 , BaO , and ZrO_2 . See ANL-6800, p. 201, Table II-1, for quantity of each oxide in mixture.

^b Nominal 60 mesh (manufacturer's designation) from which -170 mesh fraction has been removed.

^c At room temperature and atmospheric pressure.

^d At 500°C, atmospheric pressure.

^e Solid reaction charge contained 0.63 g plutonium.

during the fluorination period. In these experiments, the procedure was similar to that used in experiments shown in Table II-3 except that the gas velocities were insufficient to fluidize the alumina bed. Only plutonium and fission products were used as feed material in these experiments. Under the conditions given in the heading of Table II-3, the residual plutonium content of the bed after fluorination was 0.075 w/o. This value may be compared with a residual plutonium content of 0.003 w/o at fluorine rates of 6-8 liters/min, shown in Table II-3. It is concluded that inadequate plutonium removal is obtained when static-bed fluorination is used for the removal of plutonium. This conclusion is in agreement with data shown in Table II-3, where a dependence of plutonium removal on the fluorine flow rate is indicated.

Table II-4

SURFACE AREA OF ALUMINA BED AND PERCENT
CONVERSION OF ALUMINA TO ALUMINUM FLUORIDE^a

Addition- Fluorination Cycle	Fluoride Analysis of Alumina			Percent Al_2O_3 Conv. to AlF_3	Surface Area ^c of Bed (m^2/g)
	F (%)	Total g F	g F as AlF_3 ^b		
1	1.74	10.02	8.95	1.41	0.08
2	2.68	15.30	13.13	2.06	0.13
3	3.60	20.74	17.34	2.72	0.20
4	3.90	22.46	18.09	2.84	0.19
5	4.60	26.08	20.78	3.26	0.18

^a For the series of experiments listed in Section B of Table II-1.

^b This value was obtained by subtracting the fluoride due to the uranium and plutonium content of bed and the fluoride combined with fission product elements from the total fluoride as determined by analysis.

^c Surface areas obtained by BET method. The surface area of untreated 120 mesh alumina is $0.011 \text{ m}^2/\text{g}$.

e. Change in Surface Area and Fluoride Content of Alumina

It has been shown that plutonium is retained primarily on the surface of the alumina particles of the fluidized bed. Further, fine particles would be produced by the fluorination of alumina to aluminum fluoride (AlF_3), if the AlF_3 were abraded from the surface of the alumina granules. A significant increase in the concentration of fine particles in the fluidized bed could alter the fluidizing characteristics of the bed. For these reasons, samples of the bed material obtained from a series of experiments (see part B, Table II-1) were analyzed for changes in surface area and fluoride content. The results are shown in Table II-4. The relatively slow rise in AlF_3 content and the lack of continued increase in the surface area of the bed material indicate that, even with reuse of the alumina bed, no significant physical changes in the bed material are likely. The residual plutonium content of the bed appears to depend on the surface area of the bed, particularly after the first two addition-fluorination cycles. It may be tentatively concluded that the retention of plutonium on alumina after repeated use of the bed material will parallel the change in surface area of the bed material and that neither variable will rise significantly when the alumina bed is reused five to seven times.

f. Fluorination of Fuel After Treatment with HF-O₂

The results of experiments in which powdered mixtures of U₃O₈, PuO₂, and fission product oxides are fed into a heated, fluidized bed of alumina can be applied to a process in which a declad UO₂ fuel is simultaneously oxidized and fluorinated in the fluid bed. Such conditions would prevail, for example, if a Zircaloy-2 clad oxide fuel element were declad with HCl, leaving UO₂ pellets in the bed. Subsequent treatment of the UO₂ pellets would entail an oxidation of UO₂ in the lower portion of the fluid bed while simultaneously fluorinating the oxidation product (U₃O₈) in the upper portion of the fluid bed by use of fluorine.

Since stainless steel cladding and fuel element components are currently in use and since it appeared desirable to develop decladding methods suitable for combinations of stainless steel and Zircaloy, the reaction of mixtures of hydrogen fluoride and oxygen with these metals has been explored. Others* have found that the treatment of either stainless steel or Zircaloy with a mixture of HF and oxygen at elevated temperatures in a fluid bed will disintegrate the claddings, leaving the reaction products dispersed throughout the alumina bed material. The fuel pellets also react with the mixture of gases, resulting in the formation of UO₂F₂, UF₄, PuF₄, and fission product fluorides and/or oxides. These products are also dispersed throughout the alumina.

Several experiments were performed in which mixtures of UO₂F₂, PuF₄ and fission product fluorides were charged directly to a fluid bed of alumina and fluorinated. In addition to the reagents mentioned, solids obtained from treatment of type 304 stainless steel with HF-O₂ were added to the bed to simulate the presence of products of the decladding step. This mixture was treated with fluorine in the fluid bed, using initially a low concentration of fluorine and gradually raising the concentration of fluorine to 100% and the temperature from 450°C to 550°C. The conditions used in the experiments and the results are shown in Table II-5. The second and third experiments recorded in Table II-5 used the same bed of alumina to which was added, after completion of the first experiment, a fresh charge of reagents to produce the feed for the second experiment. Iron oxides, originally formed during the treatment of stainless steel with HF-O₂, are converted to ferric fluoride (FeF₃) and remain in the bed. Chromium, constituting approximately 19% of type 304 stainless steel, probably remains in the form of oxide after the HF-O₂ treatment, but is fluorinated by fluorine to a volatile fluoride, possibly CrO₂F₂ or CrF₅. Preliminary indications show that approximately 30-40% of the chromium and 100% of the iron remained in the bed after fluorination.

These data indicate that relatively satisfactory removals of

* BNL, unpublished results (1964).

Table II-5

FLUID-BED FLUORINATIONS OF MIXTURES OF UO_2F_2 , PuF_4 , FISSION PRODUCT FLUORIDE
AND FERRIC OXIDE

Fluorination Periods

1st Period: 450°C, 1 hr, 5-20% F_2 (once-through)
4 hr, 100% F_2 (recycle)
2nd Period: 500°C, 5 hr, 100% F_2 (recycle)
3rd Period: 550°C, 10hr, 100% F_2 (recycle)

Gas Flow Rate: 8 liters/min

Addition- Fluorination Cycle	Feed Material ^a					Retained on Alumina Bed				% of Total Pu Volatilized ^e
	Pu (g)	U (g)	F.P. (g) ^b	Fe_2O_3 (g) ^c	Al_2O_3 (g) ^d	Pu (w/o)	Pu (g)	U (w/o)	U (g)	
1	1.252	254	2.28	45.0	570	0.0087	0.053	0.041	0.240	95.8
1	0.943	191	1.71	33.8	428	0.010	0.048	0.012	0.056	94.9
2	0.943 (1.886) ^f	191	1.71	45.0	455	0.014	0.069	0.033	0.165	96.3

^a Mixture of PuF_4 , UO_2F_2 , fission product fluorides, iron oxides, and alumina.

^b Prepared by fluorination of a mixture of 10 oxides listed in footnote c, Table II-1.

^c Prepared by the $\text{HF}-\text{O}_2$ reaction with type 304 stainless steel.

^d Type T-61 alumina having a median particle size of about 150μ (100 mesh) and a particle size range of 80 to 250μ (60 to 170 mesh)

^e Based on plutonium remaining in alumina bed and total quantity of plutonium fed to reactor.

^f Cumulative plutonium added throughout this experiment.

plutonium from a bed containing decladding products may be anticipated. If the plutonium concentration observed in the third experiment (Table II-5) were to be maintained for a total of seven additions to the bed, the fractional removal of plutonium from the bed would be 99%. This conclusion is similar to that obtained from experiments (Table II-1) in which the reagent mixture was pneumatically fed to the fluid bed. These results, although preliminary in nature, indicate that adequate removal of plutonium from the alumina could be obtained, independent of the manner in which the fuel is introduced into the fluid bed and hence independent of the method of decladding.

During the course of experiments using the 1 1/2-in. dia. fluid-bed system, several types of operational problems developed. One of the major problems involved the elutriation of fine particles from the fluid bed into the disengaging section. In order to overcome these difficulties, a 2-in. dia. fluid bed system has been constructed and installed in a glovebox (see Figure II-3). This reactor will be used to study the oxidation and fluorination of pellets of UO_2 containing plutonium and fission products. Preliminary experiments in the 2-in. dia. reactor on pellets of UO_2 which did not contain plutonium or fission products indicated that satisfactory conversion of UO_2 to UF_6 can be obtained by the two-zone technique in which the pellets are oxidized to U_3O_8 by oxygen in the lower portion of the reactor and the U_3O_8 is converted to UF_6 by fluorine in the upper portion of the reactor. This technique, applicable to Zircaloy-clad fuel declad by HCl , will be applied to pellets containing plutonium.

2. Reaction of PuF_6 and Metal Fluorides

A brief examination of the sorption of PuF_6 on several metal fluorides was made, owing to the interest, generated by reports from other laboratories, in sorption techniques for the separation of UF_6 and PuF_6 . Results of experiments carried out at temperatures between 25°C and 100°C indicate that the capacity of calcium fluoride (CaF_2), lithium fluoride (LiF), and sodium fluoride (NaF) for PuF_6 , expressed as moles of PuF_6 per square meter of surface area of the metal fluorides decreases in the order $\text{NaF} > \text{LiF} \gg \text{CaF}_2$. The sorptive capacity of CaF_2 for PuF_6 was found to be very low (0.0013 mole PuF_6/m^2), indicating that CaF_2 would not be suitable for process use. The other fluorides need to be evaluated further before conclusions on their utility can be made. In none of the experiments was the observed molar ratio of metal fluoride to PuF_6 indicative of the formation of simple compounds. It should be noted, however, that formation of complex compounds of UF_6 is generally not complete unless the metal fluoride is dispersed in an inert solvent. Experiments with metal fluorides and PuF_6 using such dispersions may be carried out in the future.

3. Behavior of Molybdenum in HF-O_2 and in Fluorine

Volatilization of fission product molybdenum from the fluid bed has

Figure II-3

TWO-INCH DIAMETER FLUID-BED REACTOR INCLUDING
DISENGAGING AND FILTER SECTION

been anticipated on the basis of the known volatility of molybdenum hexafluoride (MoF_6) and the assumption that the hexafluoride is formed during fluorination. On the other hand, experiments, carried out in the 1 1/2-in. dia. fluid bed, in which MoO_3 was added to the feed material, indicated that during fluorination a compound of molybdenum was formed which had a volatility significantly lower than that expected for MoF_6 . A series of exploratory experiments was performed in which MoO_3 was treated at 450°C with mixtures of fluorine and either nitrogen or oxygen. Results indicated that little (3-5%) of the MoO_3 was converted to MoF_6 and that most of the product was a slightly volatile (at 25°C) white solid which was probably a mixture of MoF_5 and MoOF_4 . Similar results were obtained by treatment of MoO_2 with mixtures of fluorine and oxygen. That the low yield of MoF_6 was not due to reaction of oxygen and MoF_6 at 450°C was demonstrated by the lack of observable reaction when MoF_6 and oxygen were simultaneously passed through a tube heated to 450°C .

The reaction of MoO_3 with a mixture of HF and oxygen at 550°C produced a slightly volatile material which sublimed from the reactor. The volatile solid is probably MoO_2F_2 (subl. pt. 270°C). No MoF_6 was observed. It may be concluded that compounds of molybdenum will be volatilized from the fluid-bed reactor during the decladding treatment with HF- O_2 and possibly also during the fluorination step. The relative quantities of the volatile MoF_6 formed during either of these steps should be low and hence there may be only minimal molybdenum contamination of the hexafluoride product prior to purification.

4. Fluorination of Plutonium-Containing Solid Wastes from Rocky Flats

A series of experiments was carried out to determine the applicability of fluoride volatility techniques to the recovery of plutonium from solid waste materials. Samples of several types of wastes generated at Rocky Flats were subjected to fluorination, and the plutonium remaining in the residue was determined. The samples were reacted in a horizontal tube furnace by flowing elemental fluorine over the heated solid. The results of the experiments are shown in Table II-6. No obvious explanation is available for the low plutonium removal in the first experiment in which incinerator ash was fluorinated for 5 hr at 550°C .

On the basis of the results, it appears that fluorination of plutonium present in the waste samples will reduce residual plutonium concentration to acceptable levels. No experiments were carried out on the conversion of PuF_6 to PuF_4 , but information available in the literature indicates that this step should not be a problem.

Table II-6

PLUTONIUM REMOVAL FROM WASTE MATERIALS

Fluorinating Gas: Fluorine

Pressure: Atmospheric

Material	Sample Weight (g)	Pu in Sample (mg)	Reaction Time (hr)	Temp (°C)	F ₂ Flow (ml/min)	Pu in Residue (mg)	Plutonium Removal (%)
Skull Oxide	2.0795	1811.9	9	500 ^a	100 ^a	3.4	99.8
Skull Oxide	4.1120	3582.8	10	500	200	25.5	99.3
Skull Oxide	3.6811	3207.3	5	550	200	35.3	98.9
Incinerator Ash	2.2087	256	5	550	200	45.5	82.2
Incinerator Ash	2.2677	263	5	550	200	4.3	98.4 ^b
Incinerator Ash	2.2103	256	10	550	200	1.7	99.3 99.1 ^b
Sweepings	2.151	1265	5	550	200	0.6	99.9
Sweepings	2.1365	1256	10	550	200	0.4	99.9

^a The fluorination procedure for this sample was:1 hr at 370 to 510°C, F₂ flow rate 100 ml/min;4 hr at 510°C, F₂ flow rate 100 ml/min;4 hr at 490°C, F₂ flow rate 500 ml/min.^b Includes leaching of dissolution residue to remove all plutonium for analysis.

B. Engineering-Scale Investigations

1. Processing of Nuclear Reactor Fuel of Low Enrichment

Development work on a volatility reprocessing method for low enrichment fuels is in progress. Representative of these fuels is the type used in commercial power reactors, ceramic uranium dioxide (UO_2) pellets contained in Zircaloy or stainless steel tube clusters. The spent fuels will contain sufficient plutonium to warrant its recovery. Work is proceeding, then, on a process for recovering both the uranium and plutonium.

The process involves the following steps:

- a) Decladding,
- b) Fluorination of the pellets to a mixed hexafluoride product (UF_6 - PuF_6),
- c) Separation of the plutonium as the tetrafluoride (PuF_4) through the use of thermal decomposition, and
- d) Fractional distillation to provide a decontaminated UF_6 product.

Process alternatives include a fluid-bed conversion step in which a decontaminated UF_6 - PuF_6 mixture is converted to dense mixed-oxide (UO_2 - PuO_2) particles by reaction with steam and hydrogen. A similar conversion has been demonstrated with uranium alone (see ANL-6766, pp. 79-81). Distillation also provides a means of concentrating the PuF_6 fraction in the UF_6 - PuF_6 mixtures to levels of interest (10-20%) for fast reactor applications.

a. Engineering-Scale Alpha Facility

An engineering-scale alpha facility (described in ANL-6875, pp. 93-94) has been newly completed and will be used to demonstrate the steps required to carry out the fluoride volatility process. Nonirradiated materials will be used in the demonstration runs. Installed in the facility, to date, are two processing systems, a fluorination pilot plant for processing batches of UO_2 - PuO_2 pellets to the hexafluorides and a second fluid-bed unit (referred to as the converter) for demonstrating both the thermal decomposition of PuF_6 to PuF_4 and the conversion of mixed hexafluorides to oxides. This unit will facilitate the avoidance of the storage of plutonium as the hexafluoride which suffers from alpha decomposition (1-2% per day in the condensed phase). Either the oxide or tetrafluoride, which are both stable, is then stored.

Design work on a distillation column for studies with UF_6 - PuF_6 mixtures has been initiated. Installation of this unit is planned for the latter part of 1965.

During the current year, all of the units associated with overall facility operations, such as the process-gas and ventilation-gas scrubbers, ventilation controls, and refrigeration system, were completed and checked

out as being operational. The fluorine recycle pump also performed satisfactorily in pre-operational tests. Detailed operating manuals (SOP's) have been prepared for the operation of the overall facility systems and the two processing units.

Shakedown Testing of Fluorination Pilot Plant

Shakedown work with uranium alone has started in both the fluorinator and converter. This work is being conducted with windows and gloves in place in order to simulate the conditions when plutonium will be present. In addition to providing the means of checking on the performance of the various process systems, this phase of the operations serves as a training period for the operating personnel. Final sealing of the neoprene window moldings will be carried out upon completion of these shakedown tests. Work with plutonium will then commence.

One experiment, Run UO-1, involving the processing of a batch of UO_2 pellets by the oxidation-fluorination procedure has been completed in the fluorination pilot plant. In this procedure chemical pulverization occurs as the UO_2 pellets are oxidized to U_3O_8 by an oxygen-nitrogen mixture in the lower zone of the fluid bed of inert solids. The U_3O_8 , as fine particulate solids, generally less than 325 mesh, is transported by the fluidizing gas into the bed region above the pellets where fluorine is introduced and reaction to the hexafluoride occurs. The charge to the 3-in. dia. fluorinator consisted of 2.2 kg of UO_2 pellets (3-in. depth) and a 24-in. deep bed (5.52 kg) of -60 +170 mesh fused alumina. In addition to the fluorinator, the auxiliary filters, the hexafluoride collection system,* and the off-gas cleanup system were used in this experiment. The fluorine recycle pump was not operated because once-through gas flow was used.

The conditions and sequence of operations for the run are listed in Table II-7. The run was divided into four parts: (a) normal two-zone operation (oxygen in at the bottom, fluorine in at the side) until approximately 90% of the UF_6 was collected, (b) fluorine flow was continued, but admitted at the bottom at a low (5-10 v/o) concentration, with no oxygen added, (c) a period at a higher temperature, 515°C instead of 450°C , and (d) a period with higher fluorine concentrations, to 60 v/o, achieved by gradually replacing the nitrogen diluent with fluorine. Ideally, the rates of the two input reactants, oxygen and fluorine, during the main reaction period (part a) are such that the accumulation of U_3O_8 fines in the reactor is minimized. Potential problems with high filter loads (excessive pressure buildup in the reactor) are thereby avoided. Manual control of the input reactants during the current experiment was quite successful in achieving this operating condition. Automatic blow-

* The UF_6 collection system includes two large inverted-U shaped cold traps; however, only one cold trap was in use during this preliminary period.

Figure II-4

UF₆ PRODUCTION RATE AND PERCENT OF CHARGE COLLECTED
DURING RUN UO-1

increasing the duration of the blowback pulse, mechanical jarring of the upper (disengaging) sections of the unit, and increasing the temperature of the disengaging section to 350°C (Points 3 and 4). (During the earlier parts of the run, the disengaging section was kept at 250-275°C.) The filter chambers were kept at 150°C throughout the run. Increasing the concentration of fluorine in the inlet gas stream by decreasing the flow of diluent nitrogen (Point 5) gave no detectable change in the rate of UF₆ formation. The peak UF₆ production rate of 975 g/hr corresponds to 42 lb/(hr)(sq ft).

Analysis of the alumina bed after fluorination showed a residual uranium content of 0.03 w/o, equivalent to about 0.08% of the uranium charged to the reactor. Subsequent refluorination of a portion of the alumina bed under static-bed conditions in a bench-scale (1 1/2-in. dia.) reactor at 500°C and 550°C for consecutive 1-hr periods reduced the uranium content to less than 0.01 w/o.

The overall fluorine efficiency for the run was 32%. During peak production periods, efficiencies of fluorine utilization, as measured by the conversion to hexafluoride, of 72-73% were observed. The values for the fluorine concentration in the off-gas as indicated by the thermal conductivity apparatus agreed well with those calculated on the basis of fluorine input and hexafluoride production rate. This agreement indicates that little if any accumulation of intermediate uranium fluoride fines occurred during the run.

Table II-8

URANIUM MATERIAL BALANCE - RUN UO-1

<u>Uranium Distribution</u>	<u>UF₆ Equivalent</u>	
	<u>g</u>	<u>%</u>
<u>Uranium Charged</u>		
2200g UO ₂	2868	100
<u>Uranium Collected</u>		
Cold Trap	2770	96.62
Back-up NaF Trap	55	1.91
<u>Uranium Remaining in the Reactor</u>		
Final Alumina Bed (0.03 w/o U)	2.4	0.08
Unreacted Pellets (plus 40 mesh)	6.0	0.21
Fines from Filters and Filter Chambers	<u>34</u>	<u>1.18</u>
Total Uranium Accounted For	2867	99.97

The uranium material balance for the run is shown in Table II-8. From weight changes and analysis of bed residues, a material balance of 99.97% was achieved. The efficiency of the cold trap for UF₆ collection was 98%, based on the amount of material collected in the cold trap and the amount collected in the NaF back-up trap downstream of the cold trap. During the collection period the cold trap was operated at an outer wall temperature of 25 to 50°C, while the coolant temperature ranged from -64°C to -78°C.

Subsequent to the fluorination run, the material that had been collected in the cold trap was transferred to a product receiver -- a 4-in. dia. container, 2.5 ft tall. This transfer involved (1) evacuation of the cold trap and the product receiver (during this step, the cold trap is chilled and the receiver is heated), (2) chilling of the product receiver to -60°C and heating of the closed cold trap to 75 to 80°C to liquify the UF₆, and (3) a closed-system vapor transfer of the UF₆ to the chilled product receiver.

In a 2-hr period, 2587 g out of a possible 2770 g* was transferred from the cold trap and collected in the product receiver. Pumping on the warmed cold trap for an additional 3 hr resulted in the transfer of an additional 112 g of UF_6 out of the cold trap, giving a total of 2699 g. The percent transferred for the two steps was therefore 97.4, which is considered satisfactory for such an operation in a shakedown period.

The operation of the equipment, the gas control systems, the air-water cooling system on the reactor, and the thermal conductivity gas analysis apparatus were excellent. Minor difficulties were experienced with the remote-reading scale mechanism. Final closing of the alpha boxes will commence upon completion of one or two additional experiments with uranium. Work with UO_2 - PuO_2 will then start.

Converter

The converter process equipment includes gas supply sources, a gas preheater, a fluid-bed reactor with integral filter section, a secondary filter, an off-gas analysis system, an exit gas scrubber, and dry chemical traps. The reactor is fabricated of Inconel; other equipment and lines are of nickel and Monel. The unit as installed in the large alpha box is shown in Figure II-5.

The reactor is composed of three sections connected by flanges: a 60° cone bottom, a 2-in. dia. fluid-bed section and a 4-in. dia. cooling-filtering section. The cone bottom has an opening at the apex for the gas feed; the hexafluoride mixture enters through a 0.125-in. ID nozzle extending 2 1/2 in. into the cone; the fluidizing nitrogen or steam and hydrogen reactants enter through the annulus around the hexafluoride nozzle. The side opening in the cone bottom is for product take-off and sampling.

Control, indicating, and recording instruments are mounted on a panelboard adjacent to the fluorinator control panel. A hydrogen detection system is provided to monitor the air environment of the converter installation. The HF content of the process off-gas is measured by a thermal conductivity cell and is recorded continuously.

The first experiments in the converter, aimed at establishing the operating characteristics of the unit, will be hexafluoride-to-oxide conversions using a UF_6 feed and steam and hydrogen as reactants. The unit will also be used as a fluid-bed column in studies on decomposition, which was studied previously on a laboratory scale (see ANL-6766, p. 85) for separating the plutonium, as the tetrafluoride, from UF_6 - PuF_6 mixtures. The converter and fluorinator off-gas systems are manifolded to permit use of the UF_6 cold-traps during the thermal decomposition studies.

* The amount of UF_6 collected during the fluorination period according to the scale readout.

Figure II-5

FLUID-BED CONVERTER MOUNTED IN THE LARGE ALPHA BOX

Control of UO_2 Particle Size During Conversion of UF_6 to UO_2

A characteristic of the fluid-bed process for converting volatile hexafluorides to dense oxide particles is particle growth. Continuous operation of the converter is thereby limited by the growth of the particles to a size which cannot be conveniently fluidized. Resizing of the bed material through grinding and sieving or by other methods is therefore needed. For mixed uranium-plutonium systems such as those intended to be used in the engineering-scale alpha facility, it is desirable to handle these materials as little as possible. An oxidation-reduction technique for achieving in situ size reduction was demonstrated in fluid-bed conversion studies with UF_6 alone in a 3-in. dia. reactor. Particle breakup occurs as the material is oxidized to U_3O_8 .

Operating conditions for the oxidation-reduction cycle were first established using relatively small beds (1.0 to 1.5 kg) of +80 mesh (177μ) UO_2 . Oxidation was conducted at 400°C or 650°C with either 10 or 20 v/o air in nitrogen. Reduction followed at 650°C with essentially 100% hydrogen. Particle size changes were measured by means of sieve analyses of samples taken from the bed at intervals. The characteristics of the oxidized material improved, that is, smaller proportions of fines (-325 mesh) were produced, when smaller amounts of oxygen were used and when a lower temperature and a higher air concentration were used. As little as 0.25 times the stoichiometric amount of oxygen needed for complete oxidation gave the desired amount of breakup (average particle size reduced to about 1/2 the starting size).

Demonstration experiments with 6- and 12-kg beds and three complete oxidation-reduction-conversion cycles concluded this work. In each cycle, the average size of the UO_2 particle was allowed to double from about 200μ to 400μ during the hexafluoride conversion period; oxidation was then used to reduce the average particle size to its original value, and a reduction step completed the cycle. These tests showed also that particle breakup continued, but to a reduced extent, during the reduction period and in subsequent periods when fluidization was continued with only inert purge gas flowing. This characteristic of the process also must be considered in setting the final conditions for the forthcoming UF_6 - PuF_6 conversion work.

b. Decladding and Fluorination of Uranium Dioxide Fuels

Development studies are being conducted on methods of decladding Zircaloy- and stainless steel-clad UO_2 and on the fluorination recovery step of the fluid-bed fluoride volatility scheme for processing fuels of low enrichment. Applicability of this work to UO_2 -stainless steel cermet fuels is being explored. Several methods for decladding these fuels have been studied. In an oxidative-decladding method, the UO_2 pellets are oxidized to U_3O_8 fines which are separated from the cladding. Previous studies (see ANL-6875, pp. 87-88) with stainless steel tubing established operating conditions for this

method. However, mechanical operations such as broaching of the cladding or shearing of the fuel into short lengths are required, all of which are expensive to perform in radioactive environments.

Direct chemical decladding methods which do not require mechanical operations are desirable. Two methods have been considered for decladding stainless steel: (1) destructive oxidation catalyzed by hydrogen fluoride (HF), and (2) chemical destruction with aqueous hydrochloric acid in an air-fluidized bed (see below). Tube-furnace experiments at Oak Ridge National Laboratory showed that destructive oxidation of stainless steel, promoted by gaseous HF, resulted in penetration rates of 67.5 mils/hr at 650°C with 40 v/o HF in oxygen. These values indicated that HF-promoted destructive oxidation as a decladding method may be directly incorporated into the fluid-bed fluoride volatility process for stainless steel-clad fuels. For Zircaloy cladding, attack with HCl as in the enriched alloy reprocessing scheme (see below) is directly applicable. Recent work at Brookhaven National Laboratory indicates that method (1), using HF-oxygen mixtures, also causes destruction of Zircaloy.

Exploratory studies with HF-oxygen mixtures were made at Argonne in conjunction with fluorination studies on UO_2 pellets. Studies aimed at optimization of the HF-oxygen decladding process are being conducted at Brookhaven. Feasibility of processing UO_2 -stainless steel cermet fuels by the HF-oxygen-fluorine cycle has also been investigated at Argonne.

Destructive Oxidation of Stainless Steel. The rate of attack of stainless steel by HF-oxygen-nitrogen mixtures was determined in studies conducted in a 1 1/2-in. dia. bench-scale reactor and a 3-in. dia. pilot-scale unit. In the bench-scale unit, penetration rate as a function of temperature was established using a type 304 stainless steel rod as a specimen in a fluid bed of sintered alumina. The penetration rates increased with increasing temperature from ~2 mils/hr at 500°C to ~33 mils/hr at 600°C using 40 v/o HF and 40 to 60 v/o oxygen (plus nitrogen) in the feed gas stream. A practical operating temperature appears to be 550°C, which gave a penetration rate of about 30 mils/hr in the fluid-bed zone. Penetration was markedly higher for the portion of the specimen immersed in the fluidized bed than for the section of the specimen exposed to the gas phase above the bed, as shown in Figure II-6. Also, in the fluid-bed region, penetration rates were highest at the end of the specimen contacted by the entering gases and decreased in the direction of gas flow. This treatment with HF-oxygen resulted in the conversion of a major fraction of the iron to $\alpha\text{-Fe}_2\text{O}_3$ and a minor fraction to Fe_3O_4 .

Pilot-scale studies in a 3-in. dia. reactor confirmed the results from the bench-scale tests for type 304 stainless steel. In a pilot-scale test with type 347 stainless steel, a lower penetration rate, about 13 mils/hr, was achieved at 550°C.

Figure II-6

PENETRATION RATES AT 550°C
OF TYPE 304 STAINLESS STEEL
ROD BY A HF-OXYGEN MIXTURE

Equipment:

1 1/2-in. dia. fluid-bed reactor

Initial Rod Dimensions:

1/2-in. dia. by 23 in. long

Initial Rod Weight:

583.9 g

Final Rod Weight:

392.4 g

Run Time:

3 hr

Composition of Feed Gas:

40 v/o HF, 40 v/o oxygen, 20 v/o nitrogen

Fluid-bed Material:

Sintered alumina

approximately one-fourth. At the end of the first hour, the length of the bundle had been reduced by somewhat over one-half. After 3 hr of decladding, the entire fuel bundle was completely disintegrated; the reaction products were found to be well mixed with the alumina bed. The bed consisted of the alumina grain, UO_2F_2 fines (-325 mesh), partially reacted UO_2 pellets, and Fe_2O_3 scale

Processing of a Stainless Steel-Clad UO_2 Fuel Bundle. A run (Run SSOX-3) in the pilot-scale reactor simulated the processing of a type 304 stainless steel-clad UO_2 fuel bundle. Decladding by reaction with a HF-oxygen mixture was followed by a fluorination step. The fuel bundle patterned after the fuel elements in the Vallecitos Boiling Water Reactor,¹ consisted of six 3-ft long tubes containing UO_2 pellets. Plugs, force-fitted into the ends of the tubes, held the UO_2 pellets in place. The bed of sintered alumina grain* extended approximately 4 in. above the fuel bundle when fluidized. The main process conditions are detailed in Table II-9.

The destructive oxidation period was of 3-hr duration. After 1/2, 1, and 3 hr of the decladding phase, the residual fuel fragments and bed were removed from the reactor for examination. Figure II-7 shows the as-charged assembly and the assembly after 1 hr of reaction time. The temperature of the fluid bed was maintained at 550°C during the first hour but was at only 450°C during the last 2 hr of operation because of heater failure.

After the first 1/2 hr of the decladding step, the length of the fuel bundle had decreased by approxi-

¹ Fowler, W. D. and J. W. Lingafelter, Design and Fabrication of High Power Density Fuel Assemblies for VBWR Irradiation Testing, GEAP-3609, Nov. 1, 1962.

* Tabular Alumina, Type T-61, manufactured by Aluminum Company of America.

Table II-9

CONDITIONS FOR DECLADDING AND FLUORINATION OF URANIUM
DIOXIDE FUELS

	<u>Pilot-Scale Study</u>	<u>Bench-Scale Study</u>
Run No.	SSOX-3	HF-13
Type of Fuel	Fuel Bundle ^a	Stainless Steel-UO ₂ cermet
UO ₂ charge (kg)	4.5	0.016
Type 304 Stainless Steel Charge (kg)	1.6	0.074
Alumina Charge ^b (kg)	7.7	0.48
<u>Destructive Oxidation</u>		
Temperature (°C)	550 ^c	550
Time (hr)	3	4
Feed Gas Composition (v/o)		
HF	43	40
Oxygen	57	40
Nitrogen	--	20
Gas Velocity (ft/sec)	0.7	0.75
<u>Fluorination</u>		
Initial Period		
Temperature (°C)	400	250
Time (hr)	6	6
Concentration of Fluorine in nitrogen (v/o)	5	2 to 90
Gas Velocity (ft/sec)	0.77	0.25 to 0.6
Final Period		
Temperature (°C)	450	550
Time (hr)	5	5
Concentration of fluorine in nitrogen (v/o)	90	95

^a Cylindrical UO₂ pellets (0.432 in. long by 0.425-in. dia) in 0.43-in. ID tubes (wall thickness, 0.02 in.).

^b Tabular Alumina, Type T-61, nominal 48-100 mesh, manufactured by Aluminum Company of America.

^c Temperature was 450°C during the last 2 hr owing to heater failure.

Figure II-7

DESTRUCTIVE OXIDATION OF A
STAINLESS STEEL-CLAD SIMULA-
TED FUEL BUNDLE AS A RESULT
OF 1-hr EXPOSURE TO 43 v/o
HF-57 v/o O₂ AT 550°C

Comparison of original bundle with
bundle after 1 hr of exposure

Close-up view showing exposed UO₂ pellets

from the tubing. The uranium fines constituted 22% of the bed material. Eleven percent of the bed was larger than 45 mesh and consisted of scale and partially reacted pellets in about a 3:1 weight ratio. Most of the pieces of scale were about 3/8 by 3/8 in. and a few were on the order of 3/8 by 3 in. The bed material was satisfactorily fluidizable for further processing.

In the fluorination phase of the run, the bed was reacted with fluorine. The temperature of the fluid bed was maintained initially at 400°C. During the first 6 hr of operation, nitrogen at a rate of 0.5 cfm (25°C and 1 atm) was introduced at the bottom of the reactor to fluidize the bed, and fluorine (0.05 cfm) diluted with recycled off-gas (0.5 cfm) was introduced into the reactor at approximately the middle of the fluid bed. This procedure facilitates control over the fluorination of the large quantities of highly reactive uranium and other fines, since, in the middle portion of the bed, the fluidizing gas bubbles are fully developed and the solids

movement is most vigorous. Dilute fluorine was fed when the bulk of the uranium fines were present. During the second part of the fluorination (5 hr), both fluorine and recycle gas were introduced at the bottom of the reactor. During this period the fluorine concentration was increased to 90 v/o. Because of heater limitations the bed temperature did not exceed 450°C during the clean-up phase of the run although a final temperature of 550°C had been intended.

During the first part of the fluorination period, 82% of the UF₆ was collected. The concentration of uranium in the alumina bed at the end of fluorination was 0.05 w/o, indicating an overall recovery of ~99.9% of the charge. All the iron oxides (including scale) were fluorinated to FeF₃ fines. The fluorine efficiency for the entire run, based on the reaction of fluorine with both the UO₂F₂ and Fe₂O₃, was 67%. The bed at the end of the run was free flowing, and no caked material was found in the bed.

Processing of Cermet Fuel Elements. An exploratory run (Run HF-13) was made in the bench-scale fluid-bed reactor to determine the feasibility of processing UO₂-stainless steel cermet fuel by the HF-oxygen,

fluorine cycle. Cermet fuels are currently being used in medium-size power plants² and are highly enriched.

A miniature fuel subassembly weighing 90 g was processed. The subassembly was made of 18 w/o UO_2 -stainless steel (type 304) cermet. Four plates, approximately 8 3/8 in. long, 1 1/16 in. wide, and 0.03 in. thick, held together by 1/16-in. dia. nickel-200 wire to give a plate spacing of 1/8 in., were used. The subassembly was submerged in a fluid bed of sintered alumina. Details of the processing conditions are presented in Table II-9. The reaction cycle consisted of a HF-promoted destructive oxidation step and fluorination of the resultant oxides. The first step was conducted at 550°C for 4 hr with a mixture of 40 v/o HF, 40 v/o oxygen, and 20 v/o nitrogen. The second step was initiated at 250°C with ~2 v/o fluorine in the feed gas stream, and completed at 550°C with 95 v/o fluorine. The total time for fluorination was 11 hr.

Complete disintegration of the subassembly was achieved in the destructive oxidation period. Greater than 99% recovery of the uranium in charge was indicated by the low concentration of uranium in the alumina at the end of fluorination, 0.005 w/o; this level corresponds to 0.2% of the uranium in the charge. The material in the fluid-bed zone was fluidizable throughout the run and was free-flowing at the end of the run. These initial results show the applicability of this processing scheme to a variety of stainless steel fuels. A few more runs are planned to optimize the operating conditions.

Decladding Stainless Steel-Clad Fuel with Aqueous Hydrochloric Acid in an Air-Fluidized Bed. Tests on the decladding of stainless steel-clad fuel by aqueous hydrochloric acid in an air-fluidized bed were concluded during this period. The purpose of this investigation was to develop a stainless steel-decladding process that would be compatible with the overall scheme of the fluid-bed fluoride volatility process for reprocessing UO_2 fuel.

Results from initial tests in a 1 1/2-in. dia. glass column indicated that decladding rates increased with increasing liquid content in the fluidized bed (see ANL-6875, p. 87). However, fluidization of the bed was satisfactory only when small amounts of liquid were used -- quantities corresponding to about 2.7 w/o of the bed. Data reported by Leva³ on fluidization quality as a function of column diameter suggest that the use of equipment of larger size might facilitate work at higher liquid contents. On the basis of this information, further tests were conducted in a 3-in. dia. glass column.

Experiments were conducted in the temperature range 80 to 100°C,

² Directory of Nuclear Reactors, Vol. IV, Power Reactors (Revised and Supplemented Edition of Vol. I), International Atomic Energy Agency, Vienna, 1962, pp. 9 to 14.

³ Leva, Max, Fluidization, McGraw-Hill Book Co., New York, 1959, p.24.

using about 1800 g of -30 +50 mesh alumina as the bed (expanded height, about 1 ft) and air as the fluidizing medium. A 1/2-in. dia., type 304 stainless steel rod, 12 in. in length, was used as the test specimen. Penetration rates were calculated from the rod weight loss by assuming uniform attack along the length of the rod. The penetration rate for the run with the highest liquid content (15 w/o) in the bed was great enough to be measured directly.

The hydrochloric acid was injected into the bed through a hypodermic needle inserted in the perforated Teflon gas distributor plate at the bottom of the column. The effective concentration of HCl in the acid in the bed was assumed to be about 20 w/o, the equilibrium value for HCl in hydrochloric acid at the nominal operating temperature (90°C), although concentrated hydrochloric acid (37 w/o HCl) was fed.

At the beginning of each run, 95 g of hydrochloric acid was injected, giving the bed an initial liquid content of 5 w/o. Liquid feed was continued during the run. Although a portion of the acid was lost by evaporation to the fluidizing gas, steady-state acid contents in the bed were maintained by adjusting both the acid and air flow rates. The actual liquid content of the bed was determined by sampling the bed and measuring the weight loss of samples dried in an oven.

The results of the current tests were in agreement with those reported earlier -- an increase in liquid content in the bed gave increased penetration rates. Further, the larger column did facilitate operations with higher liquid contents, up to 15 w/o in this case, as opposed to only about 3 w/o in the 1 1/2-in. dia. column. The overall penetration rates, however, were low, approximately 0.1 mil/hr. Still higher liquid contents might prove satisfactory. For example, an exploratory test with the bed fluidized, but in a slurry condition (26 w/o liquid content), gave a corrosion rate of 8.7 mils/hr. Since technology of such slurry systems is meager and in view of the excellent results obtained with the HF-promoted oxidation of stainless steel, current efforts on this combined aqueous-gas fluidized system are being suspended.

c. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride

High-efficiency cleaning systems for treating the environmental air in plutonium-handling facilities are necessary because of the low permissible concentrations for plutonium in air (3×10^{-8} mg of ^{239}Pu per cubic meter of air⁴). Particulate materials are satisfactorily retained by the high-efficiency AEC-type filters that are employed. Information on the behavior of volatile

⁴ U. S. Department of Commerce National Bureau of Standards Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," Washington, D. C., 1959, p.87.

plutonium materials such as PuF_6 in such environments is of particular interest in the event of accidental release. Studies on the behavior of PuF_6 released in air environments are in progress. The work is being expedited through the use of UF_6 as a stand-in for the PuF_6 .

Experiments reported earlier (ANL-6766, pp. 87-88) indicated that when pure PuF_6 (or UF_6) is released into atmosphere of ordinary moisture content, the hydrolysis reaction, $\text{PuF}_6(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow \text{PuO}_2\text{F}_2(\text{s}) + 4 \text{HF}(\text{g})$, proceeds rapidly in the gas phase, resulting in a fume (particles $< 0.1\mu$) of plutonyl fluoride (PuO_2F_2). With an excess of water present, the hydrolysis reaction is complete, producing a particulate material that is retained by the AEC-type filters. Two filters in series reduced the plutonium concentration to between 10^{-6} and 10^{-9} of the entering concentration.

Examination by X-ray diffraction of the hydrolysis product confirmed that the reaction product is PuO_2F_2 , a homolog of the compound formed by the hydrolysis of UF_6 . Because of this similarity in behavior, further experiments were therefore planned with UF_6 while new apparatus was being installed for further experiments with PuF_6 . The results of this work are expected to facilitate the confirming experiments with PuF_6 .

An understanding of the hydrolysis and filtration mechanisms is desirable in order to better evaluate and design exhaust air treatment systems. Kinetic studies were therefore initiated simulating release of dilute PuF_6 gas streams with UF_6 .

In these experiments, UF_6 in a dry gas was mixed with a wet gas and then passed through a segmented packed bed of glass beads of known surface area. Nitrogen was the diluent gas in this work. Three filter disks in series were placed downstream of the packed bed. A schematic of this equipment is shown in Figure II-8. The equipment permitted the removal of the packed bed in segments, and also individual removal of the filter disks, each of which was analyzed separately for uranium content.

Hydrolysis rates were calculated for each packed-bed segment. The rates increased with increases in the partial pressure of either water or UF_6 . In all cases a large excess of moisture over that required for complete hydrolysis was present. Rates ranging from 0.3×10^{-4} to $0.1 \text{ mg U}/(\text{hr})(\text{sq cm})$ were obtained. The highest reaction rate was less than the mass transfer rate calculated by the method of Guptha and Thodos⁵ from known physical properties, indicating that the reaction is not mass transfer limited.

Relatively high penetration of the filters was observed, the lowest value being greater than 5% of the uranium calculated to be present in the gas

⁵ Guptha, A. D., and G. Thodos, Transfer in the Flow of Fluids Through Fixed and Fluidized Beds of Spherical Particles, A.I.Ch.E.J., 8, 608 (1962).

Figure II-8

URANIUM HEXAFLUORIDE RELEASE APPARATUS

approaching the filter face. High penetration is believed to be a result of the passage of unreacted UF_6 (or a volatile intermediate) through the filter. The data showed that when the dry nitrogen with a UF_6 concentration lower than 100 ppm was mixed with nitrogen of normal environmental moisture content, the hydrolysis reaction occurred preferentially on any solid surface contacted by the gas and did not occur in the gas phase to a significant extent. Apparently, in these cases neither the packed bed of glass beads nor the filter disks provided sufficient surface for the reaction to go to completion.

To define more clearly the effects of partial pressures of UF_6 , water, and HF, the experimental data are being correlated using a semiempirical

rate equation proposed by Hougen and Watson⁶ for reactions catalyzed by solid surfaces. The following rate equation has been found to fit the experimental data from the "dilute" releases:

$$r = \frac{191.5 p_{\text{UF}_6} p_{\text{H}_2\text{O}}}{1 + 597 p_{\text{UF}_6} + 95.5 p_{\text{HF}}}$$

where r = reaction rate, mg U/(hr) (sq cm)

p = partial pressure of subscripted component at the solid surface, mm Hg.

Data from 37 bed segments were used to obtain the above correlation. Values calculated from that correlation agreed with the observed values to within a standard deviation of 26%. Since this equation was only intended for "dilute" release systems, data from eight bed segments were not used in the computation because gas-phase reaction products (fume) had collected on these segments.

Figure II-9

PuF_6 HYDROLYSIS EQUIPMENT

New experimental facilities similar to those used for the dilute UF_6 gas release experiments have been installed in a glovebox so that further work with PuF_6 can be carried out. The installed equipment is shown in Figure II-9. Through a repeated sublimation-condensation procedure, a pure PuF_6 feed was prepared. The PuF_6 was then diluted with dry air, and this mixture was then fed to the hydrolysis apparatus.

The initial experiment with PuF_6 has been completed. The conditions and results for this run, along with those for two comparable runs with UF_6 , are tabulated in Table II-10. The majority of the hexafluoride not accounted for is deposited in the mixing zone above the packed-bed. A preliminary quantitative comparison of these runs may be made by comparing the rate constants for these

⁶ Hougen, A. O., and K. M. Watson, Chemical Process Principles, Part Three, John Wiley and Sons, New York, 1947, p. 920.

Table II-10

COMPARISON OF UF_6 AND PuF_6 HYDROLYSIS EXPERIMENTS

Packed-bed column diameter: 1.5 in.
 Packed-bed area: $332 \text{ cm}^2/\text{in.}$
 Linear velocity: 9.7 cm/sec

	Run UM-14	Run SUR-2	Run PM-1
Hexafluoride (MF_6)	UF_6	UF_6	PuF_6
$p^\circ_{\text{MF}_6}$ (mm Hg)	0.00310	0.00244	0.00156
$p^\circ_{\text{H}_2\text{O}}$ (mm Hg)	0.42	0.42	0.42
Feed Rate (mg M/hr)	15.9	12.5	8.0
Run Time (min)	58.4	60.0	60.0
<u>Wt of M Collected (mg)</u>			
0-1/2 in. segment	4.3	3.0	2.35
1/2-1 in. segment	1.3	1.45	0.516
1-2 in. segment	0.70	0.94	0.141
2-3 in. segment	0.07	0.08	0.0446
1st Filter	0.048	---	0.0525
2nd Filter	0.006	---	0.00155
3rd Filter	0.0014	---	0.00241

experiments. The variation of the rate constant for these two UF_6 runs was 17%, using the lower calculated value as the basis. The rate constant for the PuF_6 run was intermediate between those for the UF_6 runs.

Rate constants determined for adjacent bed segments gave relative rates for PuF_6 hydrolysis up to about twice that for UF_6 . Overall, the rate of hydrolysis of PuF_6 was not more than twice nor less than the rate with UF_6 . More definite conclusions must await additional experimental results.

Additional experiments are planned with PuF_6 covering the range of variables used in the series of experiments with UF_6 in order to get further comparative data on uranium and plutonium systems. If the behavior of PuF_6 continues to be similar to that of UF_6 , scaled-up release experiments will be performed with UF_6 . The results of these experiments, together with those from the surface reaction kinetic experiments, will be used as a basis for the design of safe off-gas and ventilation-gas cleanup systems.

2. Reprocessing of Nuclear Reactor Fuels of High Enrichment

Fuels of high enrichment are used in mobile power reactors, research and test reactors, and seed-and-blanket reactors. The most important types of high-enriched fuels consist of uranium alloyed and clad with either aluminum or Zircaloy-2.* The process for the recovery of uranium from alloy fuels employs three principal steps in which chemical separation of the various fuel constituents is achieved by selective volatilization of chlorides and fluorides. Since the concentration of uranium in alloy fuels is low ($<10\%$), the initial step of the recovery process involves the separation of uranium from the fuel matrix, thereby freeing the uranium for subsequent recovery by fluoride volatility methods. This is accomplished by reaction of the fuel at 350°C with HCl gas while the fuel is submerged in a fluid bed of inert particles. Separation occurs through the formation of the volatile chlorides of zirconium or aluminum (ZrCl_4 or AlCl_3). Uranium is converted to solid uranium trichloride (UCl_3) and remains, for the most part, associated with the fluid-bed material. However, a portion of the UCl_3 is entrained in the gas stream and therefore a high-temperature packed-bed gas filter is employed in series with the fluid-bed reactor to insure adequate retention of the uranium within the system. The volatile chloride produced during the hydrochlorination step represents a waste stream that requires processing for convenient storage. Studies in the pilot plant facility have shown that gaseous ZrCl_4 and AlCl_3 may be converted directly to solid oxides, ZrO_2 and Al_2O_3 , by the gas-phase reaction with steam in a fluid-bed reactor.

In the second step, the uranium chloride in the fluid-bed reactor and packed-bed filter is converted to uranium tetrafluoride (UF_4) by reaction with HF . This step was adopted to avoid the production of gaseous chlorine and chlorine fluorides that would occur in the direct fluorination of UCl_3 . This step may not be required in the commercial application of the process, especially if the UF_6 product is immediately purified and decontaminated by selective sorption-desorption using beds of sodium fluoride (NaF) pellets.

Recovery of uranium as UF_6 is achieved in the third step by the reaction between UF_4 and fluorine at temperatures of 250 to 500°C . A two-

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

temperature fluorination procedure has been found highly successful in assuring high recovery of uranium as UF_6 .

Initial work on the development of a fluid-bed fluoride volatility process for enriched alloy fuels was conducted in a 1 1/2-in. dia. fluid-bed reactor. The objective of this study was to define the processing conditions for the recovery of over 99% of the uranium from aluminum-uranium and Zircaloy-uranium alloy fuels. On the basis of highly successful demonstrations in this bench-scale reactor, a pilot-plant facility was constructed to evaluate the process on a plant scale. The facility was designed to process up to 30-kg charges of Zr-U alloy and up to 10-kg charges of Al-U alloy in the form of multiplate assemblies. The pilot plant has been in operation for 18 months. The major objectives were to demonstrate (1) the recovery of over 99% of the uranium from the alloy fuel, (2) complete control of the highly exothermic reactions, and (3) reliable operation of all equipment components. Recently, a bench-scale unit has been installed in the Senior Cave of the Chemical Engineering Division, with the primary emphasis to define clearly the disposition of fission products and the total decontamination achieved in processing enriched alloy fuels which have been irradiated.

a. Bench-Scale Studies

The bench-scale studies with unirradiated fuel materials were concerned with defining the behavior of uranium in the system and with establishing conditions that would result in a minimal amount of unrecoverable uranium. The studies were directed mainly to (1) the determination of the behavior of uranium in its passage through the packed-bed filter during the hydrochlorination step, and (2) the retention of uranium by the alumina beds after fluorination.

Extensive work was carried out on the determination of the behavior of simulated fission products and minor elements in the processing of alloy fuels to provide an insight into uranium decontamination. It was observed that the disposition of these materials was that expected from knowledge of the volatility of the higher valent chlorides and fluorides. The presence of the added fission products and minor elements did not affect either uranium recovery or the operation of the processing equipment.

It has been demonstrated in the bench-scale facility that uranium recoveries of greater than 99% can be consistently achieved under a wide variety of process conditions for both zirconium-uranium and aluminum-uranium fuel materials. The operating conditions which were found suitable for processing zirconium alloy fuels are:

Bed Material:	Sintered or fused alumina (30-120 mesh size) in sufficient quantity to cover the fuel element; a somewhat coarser grade and about a 12-in. depth of alumina as the packed-
---------------	--

- bed filter.
- Hydrochlorination: Fluid-bed temperature: 350 to 450°C
 Maximum reactor wall temperature: 400°C
 Packed-bed filter temperature: 330 to 350°C
 Superficial gas velocity: ~0.5 to 0.7 ft/sec
 HCl concentration: up to 75 v/o or as high as possible while maintaining desired bed temperatures and reaction rates
 HCl requirements: about 2.5 times stoichiometric requirements
- Hydrofluorination: 1-2 hr with 25 to 50 v/o HF in nitrogen at 270 to 350°C
- Fluorination: Gradual increase in temperature from 250°C to 500°C while fluidizing with 5 to 10 v/o fluorine in nitrogen, followed by gradual increase in fluorine concentration to 90 v/o.

Thy hydrochlorination of aluminum materials may be carried out at lower temperatures because of the lower sublimation temperature of the chloride. A moisture content of up to 1100 ppm appeared to have no adverse effect on the hydrochlorination reaction or on the quantity of uranium remaining on the alumina bed after fluorination. Final fluorination with the bed in a static condition (sub-fluidizing velocities) proved successful. With this procedure, fluorine requirements may be so low as to permit elimination of fluorine recycle and the need for a recycle pump.

In order to establish the magnitude of the effects of all the processing conditions on the amount of uranium retained by the alumina bed material at the end of the fluorination step, a stepwise regression analysis⁷ of the data from the initial bench-scale studies was performed. The following empirical relationship, derived from the analysis, correlates the data with an average error of $\pm 40\%$:

$$U = 5.73 \times 10^{-5} t \left(p_{UF_6} \right)^{1.78} \frac{e^{\frac{123.8}{T}}}{r^{0.56} \left(p_{F_2} \right)^{0.70}}$$

- where U = w/o uranium in the alumina fluid bed after fluorination,
 t = the time, hr, in which the major amount (90%) of UF_6 was recovered,
 T = the bed temperature, °K, during the high-temperature fluorination period in the two-part fluorination scheme,
 p_{UF_6} = the average partial pressure, mm Hg, of UF_6 during time t,
 r = the rate of uranium recovery, lb/(hr) (lb of alumina), for the total fluorination time,

⁷ Davies, O.L., Statistical Methods in Research and Production, Hafner Publishing Co., New York, p. 191, 1958.

p_{F_2} = the maximum partial pressure, atm, of the fluorine that the alumina was exposed to.

This relationship is presently proposed for the following ranges of operating conditions:

U = from 0.002 to 0.006 w/o
 t = from 0.02 to 4.0 hr
 T = from 350 to 500°C
 p_{UF_6} = from 1.1 to 22 mm Hg
 r_{UF_6} = from 0.0016 to 0.028 lb U/(hr) (lb of alumina)
 p_{F_2} = from 0.6 to 1.2 atm

Results of this analysis indicate that those conditions which tend to increase the partial pressure of UF_6 in the gas stream result in greater retention of uranium by the alumina bed. Conditions which appear to result in low uranium retention are: (1) operating at a low bed temperature during the initial fluorination period, (2) operating with low mass velocities in the gas stream during both the hydrochlorination and fluorination steps, and (3) operating the hydrochlorination step in such a manner as to produce a low reaction rate between uranium metal and HCl. A further analysis of the results of the pilot-scale work and the preliminary results from the bench-scale reactor being used with irradiated fuels show that these data are also correlated by this relation, giving increased reliability to its form. A topical report (ANL-6829) of these bench-scale development studies has been published.

b. Processing of Alloy Fuels on a Pilot Plant Scale

The final series of pilot plant experiments has been completed in which recovery of uranium from simulated enriched uranium alloy fuel subassemblies by the fluid-bed fluoride volatility process was demonstrated. During this program, a total of 18 runs were made wherein 24 normal uranium alloy fuel elements were processed. The facility (see ANL-6766, pp. 78-79 and ANL-6875, pp. 83-85) was designed to process up to 30-kg charges of zirconium-uranium alloy and up to 10-kg charges of aluminum-uranium alloy in the form of multiplate subassemblies (see Figure II-10).

The pilot plant facility consists of a 6-in. dia. nickel fluid-bed reactor, a 9-in. dia. packed-bed filter, a 6-in. dia. stainless steel pyrohydrolysis reactor, sodium fluoride traps for the collection of the UF_6 product, and equipment for the disposal of gaseous reagents. A summary of operating conditions for the processing of both types of alloy fuels is shown in Table II-11.

By employing a continuous hydrogen analyzer in the off-gas system during the hydrochlorination reaction, it was possible to monitor closely the progress of the reaction between the alloy metal and the HCl gas. Thus, it was possible to determine exactly when all of the fuel material had reacted.

Figure II-10

SIMULATED URANIUM-ALLOY SUBASSEMBLIES USED IN
VOLATILITY PILOT PLANT

From hydrogen analysis data, it was observed that the hydrochlorination reaction proceeds in two parts -- a constant-rate period until approximately 70% of the alloy has reacted, followed by a period during which the rate continually decreases until all the alloy has reacted. During the constant-rate period, the HCl utilization is constant; during the falling-rate period, the utilization efficiency decreases markedly. Therefore, by adding additional charges of alloy at the time when the reaction rate begins to diminish, a significant increase in the overall average reaction rate and overall average utilization efficiency can be realized. This concept was evaluated in Run 15, Table II-11. In this case, three Zircaloy-uranium fuel subassemblies were successively charged to the fluid-bed reactor. The processing method involved charging the fuel subassemblies when about 60% of the previously charged material had reacted with HCl. A photograph of a partially reacted subassembly appears in Figure II-11. By use of the successive charging technique, a significant increase in HCl utilization efficiency and average reaction rate was observed, compared to values obtained in processing a single-subassembly Zircaloy-U charge (Run 13).

During the initial runs with aluminum alloy fuels, caking of the upper layer of the packed-bed filter occurred during the fluorination step.

Table II-11

OPERATING CONDITIONS FOR FLUID-BED FLUORIDE VOLATILITY
PROCESSING OF UNIRRADIATED, URANIUM-ZIRCALOY AND
URANIUM-ALUMINUM FUEL SUBASSEMBLIES

<u>Inert Bed Material</u>				
Fluid-Bed Reactor (6-in. dia.):	40 kg Alcoa T-61 alumina (28-100 mesh) 48-in. static bed height			
Packed-Bed Filter (9-in. dia.):	16 kg Alcoa T-61 alumina (14-48 mesh) 11 to 12 in. bed height			
Pyrohydrolyzer (6-in. dia.):	10 kg of final bed from the previous run with similar fuel (i.e., with A1-U or Zircaloy-U) 20-in. static height			
<u>Run Charge</u>	<u>Run 12</u>	<u>Run 16</u>	<u>Run 13</u>	<u>Run 15</u>
Alloy Type	A1-U	A1-U	Zircaloy-U	Zircaloy-U
Weight (kg)	5,962	6,025	12,720 (9 plates)	20,380 (15 plates) 20,972 (16 plates) 15,038 (11 plates) 56,390
Uranium (g)	280.5	273.6	117.0 ± 4	546.0 ± 10
<u>Hydrochlorination</u>				
Reaction Rate (kg/hr): Avg	0.92	0.87	1.39	2.06
Max	2.8	1.4	3.0	3.3
Reaction Time (hr)	6.5	6.9	9.2	27.4
Utilization Efficiency (%): Avg	37.4	43.2	22.1	33.5
Max	65.0	67.0	53.0	59.0
<u>Temperatures (°C)</u>				
A. Hydrochlorination Step				
Reactor Bed: Avg	360	364	360	372
Max	366	408	388	403
Element Channel: Avg	—	380	370	377
Max	—	520	424	428
Reactor Wall	350	351	347	355
Packed-bed Filter	197	335	346	365
Pyrohydrolyzer Bed	326	355	333	355
B. Hydrofluorination Step (2 hr)				
Reactor Bed	360	349	357	360
Filter Bed	350	362	354	353
C. Fluorination Step				
Reactor Bed and Packed-bed Filter				
(1) Reactor Fluidized	250-500°C (7.5 hr)	250-500°C (2.8 hr)	250-500°C (6.2 hr)	250-500°C (2.4 hr)
(2) Reactor Static	500°C (2.0 hr)	500°C (3.0 hr)	500°C (2.1 hr)	500°C (2.1 hr)
<u>Reactant Concentrations (v/o)</u>				
A. HCl in N ₂	91	83.3	85	79
B. HF in N ₂	21	20	35	17.5
C. F ₂ in N ₂				
(1) Reactor Fluidized	5	4.6	4.6	4.6
(2) Reactor Static	68	68	68	68
<u>Gas Velocity in Fluid-bed Reactor (ft/sec)</u>				
A. Hydrochlorination	0.39	0.40	0.44	0.42
B. Hydrofluorination	0.41	0.40	0.38	0.49
C. Fluorination				
(1) Reactor Fluidized	0.39	0.40	0.40	0.40
(2) Reactor Static	0.04	0.04	0.04	0.04

Figure II-11

URANIUM-ZIRCONIUM SIMULATED FUEL SUBASSEMBLIES

This behavior was attributed to the accumulation of condensed iron chloride on the upper surface of the filter bed. Iron is an impurity in the aluminum alloy fuel. The iron chloride, when contacted with fluorine, reacted rapidly and sintered into a crust. To avoid this occurrence the filter bed temperature during hydrochlorination was increased from 200°C in the earlier runs to 335°C to prevent condensation and accumulation of iron chloride on the filter. At the higher temperature, the packed bed filter did not cake, but uranium losses through the filter increased substantially. It is hypothesized that a larger fraction of the more volatile higher chlorides of uranium are formed at the higher temperature in the presence of aluminum trichloride gas, and that the volatile uranium chlorides passed through the filter. For aluminum alloy fuels it appears essential, therefore, that the filter bed be maintained at temperatures near 200°C . Caking due to iron chloride condensation may be avoided by passing the gas through a small fluidized bed of alumina at 200°C upstream of the packed bed filter. The iron chloride would be expected to deposit on the fluidized-bed particles as thin layers without caking.

Several significant results from the pilot plant program are:

- (1) During the hydrochlorination step, processing rates near 3.0 kg/hr for both zirconium and aluminum alloy fuel assemblies were achieved. By cooling the reactor wall during the hydrochlorination step with an air-water mixture, it was possible to maintain nearly isothermal conditions within the reactor even during periods of high reaction rates.
- (2) By incorporating a packed-bed filter depth greater than 9 in., the level of uranium particulate material passing through the packed-bed filter was kept to less than 0.2% of the uranium in the charge.
- (3) Uranium recoveries of over 99% were obtained by employing

Table II-12

URANIUM BALANCE FOR A PILOT PLANT RUN

	<u>Weight (g)</u>	<u>Total Wt (g)</u>	<u>%</u>
<u>Total Uranium Charge</u>		841.3	100
<u>U Recoverable</u>		836.0	99.3
In UF ₆ Trapping System	832.9		
In Bed Samples	3.13		
<u>U to Waste Streams</u>		4.7	0.6
To Pyrohydrolyzer	3.17		
To Reactor Bed	0.62		
To Filter Bed	0.9		
To Scrub System	0.001		
<u>U Accounted For</u>		840.7	99.9

a two-temperature fluorination procedure in which the initial stage of the reaction is conducted at 250°C with 1 to 4 v/o F₂ in nitrogen, followed by a gradual increase in bed temperature to 500°C. The reaction is completed at 500°C with 30 to 80 v/o fluorine. A typical uranium balance for a pilot plant run is shown in Table II-12.

(4) Operational performance of the pilot plant equipment and instrumentation was entirely satisfactory throughout the program. In particular, the performance of the pyrohydrolysis fluid-bed reactor was trouble-free. Although the oxide product of this reactor was in the form of fine (-200 mesh) particles which are usually considered undesirable in the operation of fluid-bed systems, the presence of these fine particles did not affect the operation of the equipment.

The major tasks remaining in the pilot plant program are the inspection and evaluation of the pilot plant equipment and instrumentation and the correlation of corrosion data obtained during the 18 runs.

c. Bench-Scale Studies with Irradiated Fuels

Process studies with irradiated fuel materials have started in the bench-scale unit (1 1/2-in. dia. reactor) installed in the Chemical Engineering Division Senior Cave during this past year. All equipment components have been designed for completely remote operation and maintenance with manipulators. Fuels of various types including high-enrichment uranium-Zircaloy and uranium-aluminum alloys and low-enrichment ceramic uranium oxides are being used to investigate (1) the distribution of fission products throughout the various process steps, (2) decontamination factors that may be realized, and (3) the effects, if any, of irradiation and the presence of fission products on uranium recovery and reaction rates.

A schematic of the equipment and process flowsheet is shown in Figure II-12. The equipment, prior to its installation in the cave, is shown in Figure II-13. Most of the features of the bench-scale unit, in which the

Figure II-12

Figure II-13

FLUORIDE VOLATILITY APPARATUS USED IN THE
HIGH-ACTIVITY-LEVEL STUDIES ON IRRADIATED FUEL

processing of unirradiated uranium alloy fuel studies were conducted, were incorporated in this facility. The facility consists of a 1 1/2-in. dia. fluid-bed reactor and a packed-bed filter with associated equipment for the containment of volatile chlorides and UF_6 produced in the process. Volatile ZrCl_4 or AlCl_3 produced by reaction of the fuel alloy with HCl is condensed to a solid chloride which is readily disposed of by dissolution in dilute hydrochloric acid and subsequent solidification in cement. The UF_6 produced by reaction of UCl_3 with fluorine is decontaminated by a sorption-desorption operation in a series of four NaF traps maintained at temperatures between 20 and 400°C . The hexafluoride product is subsequently collected in a series of refrigerated traps. Disposal units for HCl and fluorine gases are included in the facility. All liquid wastes generated in the process will be solidified with Portland cement before discharge from the hot cell.

Provision is made for carrying out the hydrochlorination, hydrofluorination, and fluorination steps in processing enriched alloy fuels although the HF step has not actually been employed here. Provision is also made for conducting studies on the decladding and pulverization of low enriched ceramic UO_2 fuels with HF -oxygen mixtures.

During the current period the equipment was first assembled in a mock-up area and tested successfully in a series of eight experiments using nonirradiated fuel materials. The experimental conditions used were those established in the other bench-scale and pilot-plant work. These tests allowed a complete check of equipment performance and provided the means whereby operating procedures and techniques for the planned experiments with irradiated fuel were developed. The equipment was then installed in the Senior Cave Facility.

Experiments were conducted with both fully enriched uranium alloy fuels and low enrichment ceramic fuels. Of the total of six "hot" experiments completed in this unit, two were made with 5-yr-cooled enriched uranium-Zircaloy alloy, two with 6-month-cooled enriched uranium-aluminum alloy, and two with low-enrichment UO_2 pellets irradiated to a level of 20,000 Mwd/ton and cooled 18 months. The reaction sequence through the fluorination step was carried out satisfactorily in each case. Preliminary results on activity distribution and uranium decontamination, available only for the first Zircaloy experiment, showed that the bulk of the activity remains with the alumina beds and that some decontamination is achieved in each step of the process. Activity material balance was about 50%, indicating that some deposition of fission products on equipment and in lines had occurred. High uranium recovery from the alumina was achieved, the residual concentration of uranium being 0.007 w/o, similar to that achieved in the studies with nonirradiated materials. The off-gas treatment methods appear adequate since the release of activity to the stack was within maximum permissible limits. A major advantage of these volatility processes is considered to be the ability to process highly irradiated and relatively short-cooled fuels and future

experiments will be directed toward the processing of such fuels.

3. Corrosion Studies

Corrosion work is being carried out in support of the fluid-bed fluoride volatility process studies. The work is of two types: small-scale controlled laboratory tests in tube furnaces and in-plant exposure tests. These corrosion tests are preliminary and are intended primarily as a guide in the experimental program.

The laboratory tests, recently completed, were designed to examine the effect of short-term and long-term exposures of nickel to selected gaseous environments which were representative of gaseous environments found in fluoride volatility processing. Specimen description, test conditions, and corrosion rates are summarized in Table II-13. Each value shown represents an average value for four specimens. The environment described in Table II-13 (footnote e) is representative of the gaseous environment found in the processing of high-enriched uranium alloy; environment (3) is representative of the gaseous environment found in low-enriched oxide fuel processing; while environment (1) serves as a base-line test.

The corrosion rate of nickel-200 plate was found to be 0.9 mil/yr for an atmosphere of 50 v/o fluorine in nitrogen with the specimens held at about 475°C. The corrosion rates for the fluorine-HCl environment and fluorine-oxygen environment were found to be somewhat higher than the 50 v/o fluorine environment; but the range of values (0.9 to 4.1 mils/yr) indicates that only a small change in the corrosion rate occurs by alternating such a fluorine environment with either HCl or oxygen. These values are approximately an order of magnitude lower than those obtained in the pilot plant, indicating that the laboratory test results should be used conservatively.

A comparison of the values for the corrosion rate of nickel-200 welded with weld filler metal 61, a titanium-bearing filler (see Table II-13, footnote b), and nickel-200 welded with nickel-200 filler shows clearly that the welds made with nickel-200 filler have superior corrosion resistance in every instance. The high corrosion rates exhibited by the 61 filler metal welds are believed due to the loss in integrity of the normally protective nickel fluoride film as the titanium reacts forming a volatile material; TiOF_2 was found by X-ray diffraction in a condensed phase.

A comparison of the corrosion rates for nickel-200 plate with corrosion rates for nickel-200 welded with nickel-200 shows that the welded specimens exhibit slightly higher corrosion rates than the plate specimens. Both welded and nonwelded specimens were examined metallographically for evidence of intergranular penetration or localized attack in areas where high stress would be expected. No such evidence of such attack was found in any specimen. Thermal cycling and exposure of samples to air (containing

Table II-13

LONG-TERM CORROSION OF NICKEL-200 PLATE AND
WELDED NICKEL-200 PLATE IN GASEOUS ENVIRONMENTS

Environment	Corrosion Rate (mils/yr)								
	Nickel-200 Plate ^a			6l filler metal welds ^b			Nickel-200 welds ^c		
	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr
(1) F ₂ at 475°C ^d	0.9	0.9	0.9	1315	763	695	2.0	3.4	0.6
(2) F ₂ /HCl at 450°C ^e	2.1	1.5	0.9	67	76	70	3.3	2.2	1.1
(3) F ₂ /O ₂ at 500°C ^f	1.9	3.8	4.1	382	673	707	5.0	4.4	2.2

^a Nickel-200 plate, thicknesses 1/16 and 1/8 in., manufactured by the International Nickel Co., Inc. having a nominal composition in percent Ni 99.5, C 0.06, Mn 0.25, Fe 0.15, S 0.005, Si 0.05, and Cu 0.05. The corrosion rate was calculated by obtaining the weight loss of the specimen after defilming and assuming that the film had formed uniformly on all exposed surfaces of the specimen.

^b These specimens were made of two pieces of nickel-200 plate, 3/16-in. thick, welded together using nickel filler metal 6l and the Inert Gas Tungsten Arc (TIG) process. The filler metal is manufactured by the International Nickel Co., Inc., and has the following nominal composition in percent: Ni 93.0, C 0.15, Mn 1.0, Fe 1.0, S 0.01, Si 0.75, Cu 0.25, Al 1.50, Ti 2.0-3.5, other 0.50. The corrosion rate was calculated by determining the weight loss after defilming and assuming this was lost uniformly from the original weld area.

^c These specimens were made of two pieces of nickel-200 plate, 3/16-in. thick, TIG welded together using nickel-200 filler metal. The corrosion rate was calculated by determining the weight loss of the specimen after defilming and assuming this was lost uniformly from the total specimen area.

^d Environment (1). Specimens held at 475 ± 35°C in an atmosphere of 50 v/o fluorine in nitrogen at about 1000 mm Hg absolute. Gas velocity past coupons about 0.002 ft/sec.

^e Environment (2). Specimens held at 450 ± 10°C in an atmosphere of 50 v/o fluorine in nitrogen alternated with an atmosphere of 50 v/o HCl in nitrogen every 24 hr. System pressure and gas velocity similar to those listed in footnote "d" above.

^f Environment (3). Specimens held at 500 ± 25°C in an atmosphere of 50 v/o fluorine in nitrogen alternated with an atmosphere of 50 v/o oxygen in nitrogen every 24 hr. Flow conditions similar to those listed in footnote "d" above.

normal humidity) between periods of exposure to process environments had no marked effect on corrosion rates.

Preliminary evaluation of corrosion specimens mounted at various locations in the enriched uranium alloy pilot plant have been completed. Average corrosion rates of welded and unwelded nickel-200 and nickel-201 specimens mounted in the halogenation reactor were 0.10 mil/day in the fluidized bed region and 0.075 mil/day in the vapor space above the bed. Types 304 and 347 stainless steel coupons in the pyrohydrolysis reactor exhibited low rates of <0.04 mil/day in the fluid bed and <0.03 mil/day above the fluid bed. Inconel exhibited only about 25% lower corrosion rates than the stainless steel in the pyrohydrolysis reactor indicating that either material may be satisfactory. The test exposures ranged from 4 to 9 days and included up to 16 run cycles. There was no evidence of intergranular attack of any of the coupons.

From the tests to date, nickel is concluded to be a satisfactory material of construction for all of the volatility processes of interest. A summary report of this work has been prepared (ANL-6979, The Corrosion of Nickel in Process Environments, by A. A. Chilenskas and G. Gunderson).

4. Fundamental Fluidization Studies

Supporting fluidization studies of a fundamental nature were carried out in two areas: (1) fluidization of fine particles in the size range of less than 50 μ , a study of interest in both fuel processing schemes and particulate fuel fabrication methods, and (2) particle residence times at surfaces in contact with a gas-fluidized bed, a study basic to mass and heat transfer mechanisms in fluid-bed systems.

a. Fluidization of Fine Particles

Fluidization of fine particles is of interest in processes such as the fluorination of U_3O_8 fines, the preparation of uranium monocarbide, and the coating of reactor fuel particles. Such small particles are, in general, difficult to fluidize due to the effect of interparticle forces^{8,9} of an adhesive and frictional nature. The adhesive forces are caused by intermolecular interactions¹⁰⁻¹² between the particles, while the frictional forces depend mainly upon the surface geometry of the particles. To fluidize a particulate material, both the adhesive and the frictional forces, in addition to the

⁸ Morse, R. D., Ind. Eng. Chem. 47, 1170 (1955).

⁹ Parker, H. W. and W. F. Stevens, A. I. Ch. E. J. 5, 314 (1959).

¹⁰ Boehme, G., H. Krupp, H. Rabenhorst, and G. Sandstede, Trans. Inst. Chem. Engrs. (London) 40, 252 (1962).

¹¹ Haase, H., and B. H. Hardtke, Chem. Eng. Tech. 29, 814 (1957).

¹² Jordan, D. W., Brit. J. Appl. Phys. 5, Supplement No. 3, 194 (1954).

gravitational force, have to be overcome. The interparticle forces are generally negligible for larger sized particles ($>100\mu$), which readily fluidize. With small particles, the effect of interparticle forces becomes significant. The relationship between these interparticle forces, the fluidizability, and the quality of fluidization was investigated.

Fluidizability was quantitatively expressed as a fluidizability index which was defined as the ratio of the theoretical gas velocity at which fluidization of the solid particles begins if interparticle forces are not present, to the experimentally observed minimum gas velocity at which particle movement first takes place (incipient fluidization). The theoretical gas velocity can be calculated.¹³ When interparticle forces have to be overcome, the actual gas velocity for incipient fluidization is higher than the calculated one, i.e., the defined index is smaller than 1.

The quality of fluidization concerns the comparative behavior of fluidized beds chiefly with respect to the achievement of good solids mixing and consequently high rates of heat transfer. Heat transfer coefficients were used as a measure of the quality of fluidization, and in conjunction with pressure drop measurements were used to determine the incipient fluidization velocity.

The interparticle adhesion and friction were determined with an inclined plane apparatus similar to that described by Pecht.¹⁴ The materials studied included iron, nickel, and alumina in the range 2 to 150μ .

The fluidization index appears to be related to a force ratio which is defined as the ratio of the gravitational force, G_p , of a particle to the sum of G_p and the adhesive force, F_p . [Fluidization index = $G_p/(G_p + F_p)$]. The frictional force, found to be relatively small, is neglected. The fluidizability index was found to decrease with diminishing values of the force ratio, which means that as F_p becomes large in comparison with G_p , the material becomes more difficult to fluidize. Fluidization of spherical particles (18μ nickel, 3.3μ iron) was achieved when $G_p/(G_p + F_p)$ was not smaller than approximately 1×10^{-3} , and fluidization of irregular-shaped material (27μ alumina) was achieved when $G_p/(G_p + F_p)$ was larger than about 3×10^{-3} .

The work to date shows that the fluidizability of a material may be predicted from measurement of the interparticle adhesive force. The fluidization of fine particles may be improved by the addition of relatively large particles of about $200\text{-}\mu$ dia.

¹³ Rowe, P. M., Trans. Inst. Chem. Engrs. (London) 39, 43, 175 (1961).

¹⁴ Pecht, H., Chem. Ing. Tech. 33, 691 (1961).

b. Particle Residence Times at Surfaces in Gas-fluidized Beds

An understanding of the mass and heat transfer mechanisms in fluidized beds is needed for better design of processing systems. Fundamental to these mechanisms is the residence times of particles at transferring surfaces in the bed, such as walls and materials undergoing reaction.

Experimental and theoretical investigations have been initiated to measure the statistical distribution of particle residence times at solid surfaces in contact with a gas-fluidized bed. The objective of this work is to utilize these residence time distributions to predict heat transfer coefficients, using an equation developed at ANL by Ziegler et al.¹⁵

Residence time measurements of colored particles in a bed of white 60-mesh alumina particles were taken at the wall of a Lucite column 5 1/2 in. in diameter. Photographic techniques were employed in obtaining the measurements. Some film scanning was carried out by the CHLOE direct digital automatic reduction technique.* However, practical experimental problems precluded use of this method for accurate measurement of residence times.

It was demonstrated theoretically that the autocorrelation of the frame-to-frame statistical fluctuations in total colored particle counts, at steady-state conditions, yields the average residence time. Preliminary verification of this has been achieved experimentally. Further work is needed on determining residence time distributions as functions of physical and flow properties before correlations to transfer processes can be made.

¹⁵ Ziegler, E. N., L. B. Koppel, and W. T. Brazelton, Ind. Eng. Chem. Fundamentals, 3, 325 (1964).

* Courtesy of J. W. Butler, Applied Mathematics Division, Argonne National Laboratory.

III. HIGH TEMPERATURE REACTOR MATERIALS DEVELOPMENT

A program directed toward the development of high temperature nuclear reactor materials is under way. The general area of study will be the chemical stability of potential fuels (such as oxides, phosphides, sulfides, arsenides, and nitrides of uranium and their solid solutions) and the reactions of these fuels with hydrogen, its contaminants, and supporting refractory structural materials. These studies will be done quantitatively to yield thermodynamic and phase-diagram information. Each selected fuel-refractory metal-gas system is to be studied in an integrated way, using several methods of investigation that are mutually supporting. During the past year the experimental equipment capability for the general program has been established, for the most part. This is in accord with the plans set forth in ANL-6875, pp. 116-123. The analysis of the expected phase relationships in the uranium-oxygen system, given in that report, has been used to guide the initial experimentation. Exploratory work on the uranium-uranium monosulfide phase diagram has also been initiated.

A. Current Status of High Temperature Phase Relations and Thermodynamic Properties in the Uranium-Urania System

1. Objectives, Experimental Plans, and Recent Experimental Results

The specific objective of the studies of the uranium-uranium* system is to obtain comprehensive thermodynamic data for compositions from pure uranium to slightly hyperstoichiometric uranium.

The phase diagram for the condensed system is of importance in guiding and interpreting the thermodynamic experimentation. This work (Section III B) has advanced to the point that considerable detail can be given; the results are presented in Figure III-1. As was considered probable (ANL-6800, pp. 297-300), it has been found that uranium at high temperature can exist at compositions which are quite hypostoichiometric.

The thermodynamic properties of this system are to be determined by establishing the partial pressures of all the vaporizing species as functions of the temperature and composition of the condensed phases. Studies of the vaporization of the condensed phases through Knudsen effusion orifices or into transpiration carrier gases are in progress. The Knudsen effusion method is inherently limited to low gaseous pressures; thus, the effusion studies will be restricted to below about 2200°C. The transpiration method may possibly be

* The term uranium will be used in Section III to denote a phase of fluorite structure with composition unspecified; the symbol UO_2 will be used to denote stoichiometric uranium dioxide. The terms hyperstoichiometric and hypostoichiometric refer to the oxygen in UO_2 ; the symbols UO_{2-x} and UO_{2+x} denote hypostoichiometric and hyperstoichiometric uranium, respectively.

Figure III-1

URANIUM-URANIA PHASE DIAGRAM AT ELEVATED TEMPERATURES

pursued to 2800°C with the apparatus on hand.

The significant gaseous species in the system are U, UO , UO_2 , UO_3 , O, and O_2 . Their relative partial pressures vary considerably with the composition of the condensed phase(s). Knudsen effusion measurements yield R, the total rate of effusion of uranium-bearing species in moles per unit orifice area:

$$R = R_{\text{U}} + R_{\text{UO}} + R_{\text{UO}_2} + R_{\text{UO}_3} \quad (1)$$

The partial pressure of each species is related to its rate of effusion by,

$$P_i = R_i \sqrt{2\pi k T M_i} = a R_i \sqrt{M_i} \quad (2)$$

in which k is the Boltzmann constant, T is absolute temperature, and M_i is its

molecular weight. The total pressure, P , of uranium-bearing vapor species is then,

$$P = a \left(R_U \sqrt{M_U} + R_{UO} \sqrt{M_{UO}} + R_{UO_2} \sqrt{M_{UO_2}} + R_{UO_3} \sqrt{M_{UO_3}} \right). \quad (3)$$

Mass spectrometric investigation of the vapor effusing from Knudsen cells permits the determination of the ratios of the rates R_i . The data obtained will be most conveniently summarized by equilibrium constants for various gaseous reactions; e.g.,

These constants should be carefully determined as functions of temperature so that they may be reliably extrapolated to other temperatures.

The transpiration method measures the total pressure of uranium-bearing vapor species:

$$P = P_U + P_{UO} + P_{UO_2} + P_{UO_3}. \quad (5)$$

When this method is used it is generally desirable to employ a buffering carrier gas. In the present studies, the buffering carrier gas will consist of H_2 - H_2O mixtures of measured concentrations in order to render the system invariant by fixing the composition of the solid at each temperature. The invariance ensues from fixing the values of P_O and P_{O_2} , which are accurately calculable from well-established thermodynamic data for the H_2 , H_2O , O , and O_2 species. The individual partial pressures become explicitly calculable if the equilibrium constants for reactions such as Equation 4 are known.

A nearly complete set of measurements of total rates of effusion has been collected for the two-phase system uranium (liquid, saturated with UO_{2-x}) in equilibrium with UO_{2-x} (solid, saturated with uranium). Tentative values of the total pressures of uranium-bearing species were calculated by Equation 3 with the use of the approximation that the molecular weight of each species was the same as that of UO . The mass spectrometric results showed that this approximation was satisfactory to within a few percent. The results for the two-phase system are shown in Fig. III-2. Also shown is the vapor pressure (total for uranium-bearing species) data for solid $\text{UO}_{2.00}$ taken from the excellent study of Ackermann, Gilles, and Thorn.¹ Comparison of the curves shows that the vapor pressure over the two-phase system is an order of magnitude higher than over $\text{UO}_{2.00}$ in the range 1300 to 2000°C.

¹ Ackermann, R. J., P. W. Gilles, and R. J. Thorn, J. Chem. Phys. 25, 1089 (1956).

Figure III-2

TOTAL VAPOR PRESSURE OVER THE URANIUM-URANIA TWO-PHASE SYSTEM

Study of the equilibrium $U(\text{liquid, saturated with } UO_{2-x}) + UO_{2-x}(\text{solid, saturated with } U) \rightleftharpoons U(g), UO(g), UO_2(g)$; total pressure calculated assumes a mean molecular weight corresponding to that for UO .

A considerable number of Bendix T-O-F (Time-Of-Flight) mass spectrometric observations of the relative concentrations of effusing species have been made for the two-phase system. Qualitatively, the observations make it clear that over the two-phase system the predominant species (by about a factor of 10) is $UO(g)$, that $U(g)$ and $UO_2(g)$ are each present at conveniently measurable concentrations, and that $UO_3(g)$ is only barely measurable with the present sensitivity. When the data are evaluated and shown to be reliable, the species ratios will be used in Equation 3 to obtain partial pressure values.

The vapor pressures over urania throughout its existence range will be studied using H_2 - H_2O buffering mixtures in both the mass spectrometric and transpiration experimentation. In this work the buffering gaseous mixtures are to be equilibrated with the solid phase until constant compositions are reached. The compositions will then be established by chemical analyses.

The investigations discussed above should yield a family of isotherms of partial pressures of each of the species versus solid composition and thereby permit the calculation of the desired thermodynamic functions.

2. Development of Some Useful

Theoretical Guidelines for Experimentation

Theoretical analysis of the results of mass spectrometric measurements of gaseous species over (unbuffered) solids of composition ranging from $UO_{2.095}$ to $UO_{1.995}$ has led to an important general principle not known to have been previously put forth, and to some consequences of significance in guiding the experimentation.

Considerable variability in the gaseous species ratios P_{UO}/P_{UO_2} and P_{UO_3}/P_{UO_2} was observed in the mass spectrometer when solid uranium dioxide

samples of the same nominal composition ($\text{UO}_{2.000} \pm 0.005$) were studied. Also, at constant temperature and starting with the initial composition $\text{UO}_{2.095}$, a rapid decrease in the $P_{\text{UO}_3}/P_{\text{UO}_2}$ ratio was observed simultaneously with a rapid increase in the $P_{\text{UO}}/P_{\text{UO}_2}$ ratio as the composition changed in stoichiometry toward lower O/U atomic ratios. In general, the observations show that the relative concentrations of gaseous species are very sensitive functions of small changes in the stoichiometry of solid urania. Because of this, the following thermodynamic arguments were used to establish criteria to aid in guiding the experimentation.

It appears established¹ that urania vaporizes congruently (from an effusion cell) at a composition which, if not precisely UO_2 , is probably within ± 0.005 unit of the stoichiometric O/U ratio. There must be either a maximum or a minimum in the total pressure for the congruency condition to obtain. (The effusion condition causes only a minor effect in the system under discussion.) The data of Figure III-2 demonstrate that the total pressure of uranium-bearing species is about a factor of 10 lower over UO_2 than over the hypostoichiometric composition at the uranium-rich phase boundary. The contribution from the species O and O_2 can be shown to be negligible. Therefore, congruency occurs at a minimum pressure rather than at a maximum pressure. But the mass spectrometric results have shown that $\text{UO}_2(\text{g})$ is the major species during congruent effusion and the $\text{UO}(\text{g})$ and $\text{UO}_3(\text{g})$ are each much lower in concentration. P_{UO_2} must reach a maximum at some composition of the condensed uranium-oxygen binary system. One might intuitively expect that this composition is in the vicinity of UO_2 . There thus seems to be a possible conflict in the expected occurrence of a maximum P_{UO_2} at a solid composition near UO_2 while the vapor above it, which consists predominantly of $\text{UO}_2(\text{g})$, reaches a minimum in total pressure. It seemed worthwhile to determine, if possible, through thermodynamic arguments the solid composition at which P_{UO_2} is a maximum.

The following general equation for a condensed binary A-B system at equilibrium with its gas phase was developed by means of the Gibbs-Duhem relation and equilibrium relationships for the gaseous species:

$$\left(\frac{\partial \ln P_{A_a B_b}}{\partial \ln P_B} \right)_T = \frac{-z + \left(\frac{V_c}{RT} \right) \left(1 + \frac{b}{a} + z \right) \left[\left(\sum_{j=0}^{\infty} \sum_{i=0}^{\infty} j P_{A_i B_j} \right) - \frac{b}{a} \left(\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} i P_{A_i B_j} \right) \right]}{\frac{1}{a} \left[1 - \left(\frac{V_c}{RT} \right) \left(1 + \frac{b}{a} + z \right) \left(\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} i P_{A_i B_j} \right) \right]} \quad (6)$$

The symbols are identified as follows:

$P_{A_a B_b}$ = partial pressure in the gas phase of a particular species of the molecular formula $A_a B_b$;

P_B = partial pressure in the gas phase of the component B;

z = composition variable representing the deviation of the condensed phase from the stoichiometric b/a ration in the formulation $AB_{b/a + z}$;

V_c = molar volume of the condensed phase at the temperature T ;

R = gas constant; and

i, j = running indices representing the atoms per molecule for all possible gaseous molecules.

The equation is exact except for the assumption of ideal gas behavior. By setting the derivative equal to zero, one can show that for systems at high temperature and low pressure a maximum in $P_{A_a B_b}$ occurs when z is an

exceedingly small value, that is, the partial pressure of the $A_a B_b$ species goes through a maximum when the solid phase has the stoichiometry of that gaseous species. A maximum with respect to $\ln P_B$ also requires a maximum with respect to X_B , the gram-atom fraction of component B in the solid phase, since P_B must be a continuously increasing function of X_B . For the uranium-oxygen binary system, in the composition range encompassing the urania phase, the result of the application of Equation 6 is

$$\left(\frac{\partial \ln P_{UO_2}}{\partial \ln P_O} \right)_T = \frac{-z + \left(\frac{V_c}{RT} \right) (3 + z) (P_{UO_3} + P_O + 2P_{O_2} - 2P_U - P_{UO})}{1 - \left(\frac{V_c}{RT} \right) (3 + z) (P_U + P_{UO} + P_{UO_2} + P_{UO_3})} \quad (7)$$

The use of available order-of-magnitude data leads to z (at max.) $\approx \pm 10^{-10}$ at 2000°K.

Except at values of $z \approx \pm 10^{-10}$, the very small terms involving the volume of the condensed phase in Equation 7 may be neglected and the equation may be rewritten,

$$\left(\frac{\partial \ln P_O}{\partial \ln P_{UO_2}} \right)_T = -\frac{1}{z} \quad (8)$$

Similar equations may be derived for the other important species:

$$\left(\frac{\partial \ln P_{\text{UO}}}{\partial \ln P_{\text{UO}_2}} \right)_T = \frac{1+z}{z}, \quad (9)$$

$$\left(\frac{\partial \ln P_{\text{UO}_3}}{\partial \ln P_{\text{UO}_2}} \right)_T = - \frac{1+z}{z}, \quad (10)$$

$$\left(\frac{\partial \ln P_{\text{U}}}{\partial \ln P_{\text{UO}_2}} \right)_T = \frac{2+z}{z}. \quad (11)$$

The form of the derivatives in these expressions was chosen to permit inspection of the behavior of each species with reference to $\text{UO}_2(\text{g})$, a species whose partial pressure is known to be the least sensitive to changes in the composition of urania. Equations 8 to 11 demonstrate that the partial pressures of all the other species, however, are highly sensitive to variations in the stoichiometry of the condensed phase. This is illustrated by some recent data obtained at 2100°C . On going from solid $\text{UO}_{1.82}$ to solid UO_2 the partial pressures changed by the following factors: UO_2 , 3.64; UO , 2.8×10^{-3} ; UO_3 , 4.7×10^3 ; U , 2.1×10^{-6} .

An extreme variability of ratios of gaseous species over the solid in the vicinity of UO_2 is predicted by these equations and was observed in the mass spectrometer for different samples of nominal UO_2 . The variations may arise from composition differences too small to be discerned by existing analytical procedures. (It is, of course, worth bearing in mind that small variations in sample contamination could also produce the same effects if the contaminants were of an oxidizing or reducing character.)

On one important point the analysis given above leads to the same conclusion as do theoretical treatments² based on solid state models for non-stoichiometric compounds, namely, the partial pressure of oxygen is expected to be inordinately sensitive to small deviations in z . The point is well demonstrated in the paper by Hagemark *et al.*³ which compares the results of several investigations on hyperstoichiometric urania. Although generally good agreement is found for compositions $z \geq 0.01$, gross disagreement, even to the

² Anderson, J. S., "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, Ch. 1, p. 6.

³ Hagemark, K., KR-67, Institutt for Atomenergi, Kjeller Research Establishment, Kjeller, Norway, February 1964.

extent of opposite signs, is found for compositions $z < 0.01$.

The mathematical analysis and the observations to date have led to a better understanding of the experimental procedures which need special concern if reliable thermodynamic values are to be obtained for urania, and particularly, for nearly stoichiometric urania. First, it is important that compositions of solids be controlled to precise values during the collection of condensable vapors if the results are to be translated into equilibrium pressure values, as, for example, in transpiration measurements. Secondly, there is a need to know the composition of the solid phase with greater precision and accuracy than current limitations in chemical analysis permit.

With regard to the first of these considerations, the appropriate procedure is to make use of a buffering technique. This is one of the prime reasons for using H_2 - H_2O mixtures in the carrier gas in the transpiration measurements. Another equally important reason is that oxygen partial pressures are directly calculable from the H_2/H_2O concentration ratios used. Some of the mass spectrometric measurements will also make use of this buffering gas.

The mass spectrometric, torsion, and continuous recording effusion techniques, which give essentially instantaneous observations, may be used to circumvent the problem of composition changes during effusion; the thermodynamic analysis suggests how this may, in principle, be done through the use of Equations 8 to 11. Consider mass spectrometric measurements on the vapor effusing from solid UO_{2+z} which has initially a value of z corresponding to a point on the hypostoichiometric phase boundary. It is known that at a given temperature the value of z will continuously shift until the congruently effusing composition (very near UO_2) is reached. Thus if a continuous record of the ion intensities, I_i , of each of the two dominant species, $UO(g)$ and $UO_2(g)$, were obtained for this composition range, the slope of a $\log I_{UO}$ vs. $\log I_{UO_2}$ curve would establish the composition of the solid phase for any pair of values of I_{UO} and I_{UO_2} . This follows from the fact that I_i is directly proportional to P_i and from Equation 9. The accuracy of such a determination of composition will depend on how closely the proportionality between I_i and P_i can be held constant during the course of a run. It seems possible that this approach may permit determinations of composition with a higher degree of accuracy than is possible by chemical analysis. Edwards and Brodsky⁴ have already applied this type of thermodynamic approach for the determination of compositions to effusion systems. In their work the error in the compositions of the gas phase, as determined by chemical analysis of very small collections of effusate, was considerably reduced by the thermodynamic evaluation.

The remainder of Section III presents the status of current experimentation, classified according to the different methods being utilized.

⁴ Edwards, R. K. and M.B. Brodsky, J. Am. Chem. Soc., 78, 2893 (1956).

Figure III-3

APPARATUS FOR EFFUSION EXPERIMENTS

B. The Uranium-Urania System

1. Effusion Vapor Pressure Studies

Vapor pressure measurements in the range 1300 to 2000°C have been carried out by the effusion method for the two-phase system, uranium (liquid, saturated with UO_{2-x}) in equilibrium with UO_{2-x} (solid, saturated with uranium). This study is being conducted in collaboration with R. J. Thorn and R. J. Ackermann of the Chemistry Division. The effusion apparatus that is being used has been described elsewhere¹ and is shown in Figure III-3. Tungsten effusion cells such as that shown in Figure III-4 were used. Each cell consisted

Figure III-4

of two parts which were tightly fitted together by means of a tapered joint. The effusion cells were heated by means of an induction coil. A Leeds and Northrup optical pyrometer was used to observe temperatures in the "black body" cavity in the base of the cell. The pyrometer was calibrated by using the melting point of copper as a reference temperature and by the rotating sector method for temperatures higher than the melting point of copper. The vacuum system was pumped by a mercury diffusion pump to a gauge pressure lower than 10^{-6} torr.

The desired two-phase contact was generally established by placing uranium in urania crucibles within the effusion cells. Some of the measurements employed enriched uranium-urania mixtures in order to increase the sensitivity of analysis of the effusates. In these cases no attempt was

made to fabricate crucibles from the enriched urania; instead, contact between uranium and urania was established within a tantalum cup which was placed in the tungsten effusion cell. Effusates were collected on cooled platinum targets and the total weight of uranium-bearing species was determined by α -particle counting.

The vapor pressure was calculated by means of the equation,

$$P = \frac{W}{a} \left(\frac{2\pi RT}{M} \right)^{1/2} \left(\frac{d^2 + r^2}{r^2} \right),$$

where W is the weight of the effusing vapor per unit time, a is the area of the effusion orifice, r is the radius of the target disc, d is the distance between the orifice and the target, M is the molecular weight of the effusing species, R is the gas constant, and T is the temperature in $^{\circ}\text{K}$. The effusion orifice approximated a "knife edge" and correction for nonideality of the orifice was considered unnecessary. Another series of measurements utilizing smaller effusion orifices is in progress and, when completed, a technical report covering the entire study will be prepared.

Two measurements were carried out by an isopiestic equilibration technique to obtain compositions at the hypostoichiometric boundary of the urania phase. A tantalum crucible with a tight-fitting lid was outgassed by heating in vacuum at 2100°C for 2 hr. A thin-walled urania cup containing uranium metal was centered in this crucible. Small pellets of urania were placed in the annular space between the oxide cup and the tantalum crucible wall. The crucible assembly was evacuated ($<10^{-6}$ torr), heated slowly to the desired temperature, and held at temperature for a few hours. After cooling in vacuum, the crucible lid was opened and the oxide pellets were carefully removed and analyzed for oxygen content. The results obtained are included in Figure III-1. Some additional isopiestic equilibrations with longer reaction periods will be carried out to evaluate whether true saturation was achieved.

2. Mass Spectrometric Effusion Studies

Measurements of the relative concentrations of gaseous species in equilibrium with condensed phases of the uranium-uranium system have been undertaken. In this study, a mass spectrometer (Bendix T-O-F) is being used to determine the concentrations of the various species in the vapor effusing from a Knudsen effusion cell. Measurements have been carried out on a number of solid urania samples having different O/U ratios. The results have helped to define optimum conditions for experimentation. Several instrumentation problems were also revealed and for this reason none of the data is being reported until they are more completely analyzed for consistency. However, some of the qualitative results obtained and their theoretical implications have been discussed in Section III A 2.

3. Transpiration Studies of Vaporization

Extension of the vapor pressure measurements to higher temperatures than those possible in the effusion measurements is to be carried out by means of the transpiration method (ANL-6800, p. 302). The vaporization measurements will be made in the range 2000 to 3000°C using inert carrier gases, such as helium or argon, or reactive carrier gases, such as hydrogen or hydrogen-water mixtures.

The essential features of the transpiration apparatus are indicated in the schematic diagram shown in Figure III-5. The rhenium outer tube, the

Figure III-5

TRANSPIRATION APPARATUS

tungsten sample holder tube, and the condenser tubes are on hand. However, the initial experiments, which are being made below 2400°C , employ a less expensive alternative assembly, in which the rhenium and tungsten outer tubes are constructed of tungsten-molybdenum alloy. A Brew Model 1064* vacuum resistance furnace capable of reaching a temperature of approximately 3000°C is used for heating. Sample temperatures are observed by sighting an optical pyrometer through a hole in the condenser tube. The carrier gas manifold system includes a moisture monitor (electrolytic cell type) attached to the manifold on both inlet and outlet sides of the transpiration chamber. The volume of carrier gas used during a measurement is determined by means of a wet test meter located at the exit side of the apparatus.

Initial experiments have been carried out with solid UO_2 using argon as the carrier gas. The condensed uranium-bearing material which was collected in the tungsten condenser tube was dissolved by repeated elutions with hot concentrated nitric acid. The solutions were assayed for uranium by fluorophotometric analysis. About five measurements of the total vapor pressure of solid UO_2 have been made and the data fall very well on the appropriate curve of Figure III-2, thereby indicating that the apparatus is functioning properly.

4. Uranium-Urania Phase Diagram Studies

In an earlier report (ANL-6875, p. 121), the uranium-urania system was predicted to contain a wide miscibility gap at elevated temperatures, thereby implying the existence of a monotectic. Work reported in the literature had not been carried out at sufficiently high temperatures to establish this feature of the phase diagram. The ANL report also pointed out that a hypostoichiometric composition range for urania was probable although no work to establish the lower hypostoichiometric phase boundary had been reported.

The essential features of the diagram have since been established in this laboratory and are shown in Figure III-1. The existence of a liquid miscibility gap of substantial width was established by the metallographic examination of arc-melted alloys of a wide range of compositions. The monotectic composition

* Richard D. Brew Co., Concord, N. H.

was found to have an O/U atom ratio = 1.30 ± 0.10 (65 m/o UO_2 - 35 m/o U). The monotectic temperature was determined to be $2500 \pm 30^\circ\text{C}$ from the metallographic examination of alloys produced by heating at selected temperatures urania crucibles containing sufficient uranium to make the overall composition close to the monotectic composition. No intermediate phases in the system were found.

Figure III-6

GROWTH LAYER OF HYPOSTOICHIOMETRIC URANIA BETWEEN LIQUID URANIUM AND URANIA CRUCIBLE

Growth at 2300°C after 1/2 hr.

Specimen: as polished

Crucible: 1 in. OD

The liquidus and solidus data below the monotectic temperature were obtained from experiments in which uranium melts were equilibrated with urania crucibles in a purified helium atmosphere and then cooled rapidly to room temperature. The liquidus data, which were obtained by analysis of the uranium ingot products, are consistent with the data obtained below 2000°C

by Gray *et al.*,⁵ but are in sharp disagreement with the data obtained from 1530 to 2290°C by Blum *et al.*⁶ The solidus data, i.e., the hypostoichiometric boundary of urania, were obtained by analysis of uranium oxide growths which formed between the uranium melts and the crucibles. One such growth is shown in Figure III-6. At room temperature, these porosity-free growths were found to consist of relatively large crystals of UO_2 which contained α -uranium as a dispersed phase located at grain boundaries and within the grains. It appeared that at the temperature of the experiments the uranium had been in solid solution in the urania crystals. The separate isopiestic study (Section B-1, above) of the hypostoichiometric boundary, in which urania pellets are equilibrated via the vapor phase with mixtures of uranium and urania, gives good support to this view.

More detailed descriptions of the experimentation are available in ANL-6900, p. 215 and ANL-6925 (in press). Further work is in progress to determine the hypostoichiometric phase boundary of urania above the monotectic temperature.

C. Uranium-Uranium Monosulfide Phase Diagram Studies

Work projected in ANL-6875, p. 123 (and reported in ANL-6900, p. 219) on uranium monosulfide was concerned with the study of its diffusion through tungsten. However, the diffusion rate was found to be too low to warrant further study and led to the conclusion that dense tungsten was well suited for containing uranium monosulfide at high temperatures. Current studies are directed toward delineation of the uranium-uranium monosulfide phase diagram. Thermodynamic investigations, similar to those under way for the uranium-uranium system, will follow when the phase diagram studies are sufficiently advanced.

The liquidus boundary of the uranium-uranium monosulfide system is currently being determined. A series of arc melting experiments with pressed pellets of mixtures of uranium and uranium monosulfide has yielded no indication of a monotectic region. Measurements of the solubility of uranium monosulfide in liquid uranium were carried out in a manner analogous to the liquidus work in the uranium-uranium system. Uranium metal was equilibrated with a uranium monosulfide crucible. Compositions of the quenched liquid phase were determined by chemical analysis and gave the results shown in Fig. III-7.

⁵ Gray, A. G. and J. R. Thompson, NBS Grasselli Laboratories Progress Report on Metallurgy for December 1944, CT-2618, 1944.

⁶ Blum, P.L., P. Guinet, and H. Vaugoyeau, *Compt. Rend.*, 257, 3401 (1963).

Figure III-7

Further work on determination of the liquidus and solidus boundaries is planned.

TENTATIVE PHASE DIAGRAM FOR
THE URANIUM-URANIUM
MONOSULFIDE SYSTEM

IV. CALORIMETRY

The program of the calorimetric laboratory is directed toward the determination of thermodynamic properties of substances of interest in the fields of high temperature chemistry and atomic energy. The technique of fluorine bomb calorimetry has been developed to obtain data on the enthalpy of formation of substances not amenable to conventional calorimetry.

A calorimeter for measuring the enthalpies of compounds up to 1500°C has been designed and constructed. It is currently being tested by measurements of the enthalpy of a sample of sapphire (Calorimetry Conference standard). A calorimeter for making similar measurements up to 2500°C (using electron-bombardment heating) has also been designed; but work on its assembly was suspended during most of the past year in order to bring the 1500°C calorimeter into operating condition.

A. Fluorine Bomb Calorimetry

1. Two-Chambered Vessel

a. Phosphorus, Sulfur, and Selenium

Of considerable interest as possible reactor fuels are the phosphides, sulfides, and selenides of uranium. Their enthalpies of formation will be determined by reaction with fluorine. The enthalpies of formation of phosphorus pentafluoride, sulfur hexafluoride, and selenium hexafluoride are necessary auxiliary data whose values have been determined. The two-chambered vessel¹ that was developed for substances that react spontaneously with fluorine was used (see ANL-6875, Figure IV-2, p. 126). Samples were supported on nickel dishes for the combustions. Phosphorus pentafluoride was the only product of the phosphorus combustions. Sulfur hexafluoride was the major product of the sulfur combustions; a very small amount of a lower, unidentified fluoride of sulfur was formed, but the thermal correction for this amounted to only 0.004% of the heat evolved. Selenium hexafluoride appeared to be the only product of the combustion of selenium. The enthalpies of formation obtained in these studies are given below:

¹ Nuttall, R. L., S. S. Wise, and W. N. Hubbard, Combustion Bomb Reaction Vessel for Spontaneously Combustible Materials, Rev. Sci. Instr., 32, 1402 (1961).

The uncertainties given are equal to twice the overall standard deviations. Because the samples used were very pure, the main contributions to the uncertainties were from the precision of the calibration and combustion experiments.

b. Zirconium, Hafnium, Niobium, and Tantalum Diborides

The two-chambered reaction vessel was also used for combustions of the diborides of zirconium, hafnium, niobium, and tantalum. The technique and preliminary results of the zirconium and hafnium combustions have been discussed previously (ANL-6875, pp. 125 to 127). Additional analytical work was done on the zirconium and hafnium diboride samples in order to decrease the uncertainty in their compositions. This work led to revision of the earlier data. The revised energies of combustion and the energies of combustion of niobium and tantalum diborides are given below:

	$-\Delta E_{c298}^0$ (kcal mole ⁻¹)
$ZrB_{2.000}(c) + 5.000 F_2(g) \rightarrow ZrF_4(c) + 2.000 BF_3(g)$	920.0 ± 0.7
$HfB_{2.013}(c) + 5.020 F_2(g) \rightarrow HfF_4(c) + 2.013 BF_3(g)$	927.5 ± 1.2
$NbB_{1.883}(c) + 5.325 F_2(g) \rightarrow NbF_5(c) + 1.883 BF_3(g)$	883.5 ± 1.2
$TaB_{1.927}(c) + 5.390 F_2(g) \rightarrow TaF_5(c) + 1.927 BF_3(g)$	932.1 ± 1.2

The values derived for the enthalpies of formation were:

	$-\Delta H_f^0$ (kcal mole ⁻¹)
$Zr(c) + 2.000 B(c) \rightarrow ZrB_{2.000}(c)$	78.6 ± 1.4
$Hf(c) + 2.013 B(c) \rightarrow HfB_{2.013}(c)$	79.3 ± 2.0
$Nb(c) + 1.883 B(c) \rightarrow NbB_{1.883}(c)$	59.7 ± 1.8
$Ta(c) + 1.927 B(c) \rightarrow TaB_{1.927}(c)$	45.3 ± 1.9

The relatively large uncertainties in the results for the diborides are attributable to the imprecision of the determination of the ratio of boron to metal in the samples. Another source of uncertainty (discussed below in Section A-2a) is the value used for the enthalpy of formation of boron trifluoride.

c. General

Experiments are in progress for the purpose of verifying the equivalence of fluorine combustion results obtained by use of the two-chambered and single-chambered reaction vessels. Additional corrections are applied to the data from the two-chambered reaction vessel because of (1) expansion of fluorine into the combustion chamber, and (2) reaction(s) of fluorine at the bomb wall. Elucidation of the nature and extent of the latter correction is being sought.

Although the presently available two-chambered reaction vessel is very useful, it has the drawback that a maximum pressure of only eight atmospheres of fluorine can be introduced into the bomb. Because this pressure is insufficient to achieve the complete combustion of some substances, another two-chambered vessel is being designed for use with higher pressures.

2. Single-Chambered Bomb

a. Boron

A source of uncertainty in the work on the diborides (see Section A-1b above) is the value for the enthalpy of formation of boron trifluoride for the reaction

This value ($-269.8_8 \pm 0.2_9$ kcal mole⁻¹) was determined earlier by Wise *et al.*² in this laboratory by means of a single-chambered combustion bomb. Since then, there have been indications that the earlier work might be in error because of faulty technique or inadequate impurity analyses. Consequently, the enthalpy of formation has been redetermined. The new determination was made with a single-chambered combustion bomb using a much purer sample and an improved combustion technique and, indeed, a different value ($-271.9_3 \pm 0.2_5$ kcal mole⁻¹) was obtained. Two combustions by the improved technique and with Wise's sample yielded values (-270.7_3 and -269.7_3 kcal mole⁻¹) in good agreement with Wise's; the discrepancy, therefore, cannot be ascribed to combustion technique. Additional impurity analyses and mass spectroscopic determinations of the boron isotope ratio in each of the two samples have been made. The boron isotope ratios in the two samples are different, but not by enough to account for the discrepancy. It now appears that the major part of the discrepancy is due to an unsuspected nitrogen contamination in the original sample.

² Wise, S. S., J. L. Margrave, H. M. Feder and W. N. Hubbard, Fluorine Bomb Calorimetry III. The Heat of Formation of Boron Trifluoride, J. Phys. Chem., 65, 2157 (1961)

b. Magnesium, Yttrium, Aluminum, and Holmium

The combustion in fluorine of metals that form relatively nonvolatile fluorides presents special problems. It is necessary to carry out the combustion at high enough temperatures to volatilize the fluoride or the metal. A technique was developed in which a suspended sample is burned in a bomb lined with the fluoride of the metal. This technique (see ANL-6875, Figure IV-1, p.125) was used for combustions of magnesium and yttrium in fluorine.

The enthalpies of formation obtained were:

When this method was used for combustions of aluminum and holmium, the combustion proceeded so slowly that the burning sample fell onto the fluoride liner of the bomb, melted the liner at the point of contact, submerged, and was extinguished. The technique was therefore revised. A portion of the metal foil specimen was formed into an open box; other disc-shaped portions of the foil were placed under the box as illustrated

in Figure IV-1. The combustion then proceeded in a series of steps as each successive piece of foil ignited. The amount of unburned material which fell onto the fluoride liner was greatly reduced.

Figure IV-1

COMBUSTION BOMB FOR
ALUMINUM AND HOLMIUM

The enthalpies of formation obtained were:

The value given for the enthalpy of formation of HoF_3 is tentative.

The results of preliminary combustions indicate that the revised technique will probably be satisfactory for lanthanum, gadolinium, and nickel.

c. Silicon Carbide

The literature values³ for the enthalpy of formation of silicon carbide vary over a range of 8 kcal mole⁻¹. This laboratory is attempting to establish a definitive value by combustions of silicon carbide in fluorine, according to the reaction

The bomb and sample arrangement used are depicted in Figure IV-2. Four

Figure IV-2

COMBUSTION BOMB AND SAMPLE ARRANGEMENT FOR SILICON CARBIDE

samples were burned. Two of the samples were α -SiC, one green and the other "golden grain". The other two samples were β -SiC, one as originally prepared,

³ d'Entremont, J.C. and J. Chipman, The Free Energy of Silicon Carbide from its Solubility in Molten Silver, J. Phys. Chem., 67, 499 (1963).

and the other leached with acid to remove metallic impurities. The values obtained for the energies of combustion were:

	$-\Delta E_{c298}^0/M$ (cal g ⁻¹)
α -SiC (green)	14,722.7 $\pm$ 5.7
α -SiC ("golden grain")	14,701.2 $\pm$ 7.4
β -SiC (original)	14,722.3 $\pm$ 5.2
β -SiC (leached)	14,720.9 $\pm$ 4.4

The values obtained with the β -SiC samples are in excellent agreement with each other despite differences in impurity contents. It is reasonable to pool the data for both samples and derive the following enthalpy of formation:

This value is within the range of values summarized by d'Entremont and Chipman³ and is in agreement with a value of $-15.8 \pm 0.9 \text{ kcal mole}^{-1}$ obtained by them from equilibrium measurements.

The values obtained for the α -SiC samples are in disagreement with each other and are suspected to be subject to some undefined error. Analysis of the detailed data indicates that all the α -SiC samples burned less completely than the β -SiC samples. In order to obtain more complete combustions, an α -SiC sample with smaller particle size will be studied.

The final uncertainty in the fluorine bomb calorimetric value for the enthalpy of formation of silicon carbide will reflect any uncertainty in the enthalpy of formation of tetrafluoromethane (CF₄). The present uncertainty in the latter value is large ($\pm 2 \text{ kcal mole}^{-1}$). Because the enthalpy of formation of CF₄ is a key thermochemical datum, its direct measurement by the reaction of graphite and fluorine in a calorimeter is planned.

3. Fluorine Flow Calorimetry

When graphite was burned in fluorine by the supported-rod technique (illustrated in ANL-6875, Figure IV-3, p. 129), a polymeric white perfluorocarbon compound was formed during the extinguishment of the burning. When uranium was studied by this technique, lower fluorides were also formed toward

the end of the burning period. It appears that for certain substances, including the compounds of uranium that are of particular interest in this program, a fluorine flow calorimetric system would be advantageous. In such a system fluorine can be passed continuously over the sample until the entire sample is consumed. The formation of lower fluorides should be minimized. Additional advantages of such a system are: fluorine-sensitive compounds can be kept in an inert atmosphere until ignition is desired; the rate of reaction and the temperature in the reaction zone can be controlled by the rate of flow of fluorine into the vessel and, consequently, corrosion of the sample support dish can be minimized; and the amount of sample burned can be varied over a large range.

Figure IV-3

FLUORINE FLOW CALORIMETRIC SYSTEM

Preliminary experiments were made with mocked-up flow reaction systems. Combustions were performed with various substances, including graphite and some uranium compounds. The advantages discussed above were demonstrated. Construction and purchase of parts for a fluorine-flow calorimetric system have been started. Figure IV-3 is a sketch of the system that will be assembled.

B. Quartz-Crystal Thermometer

Platinum-resistance thermometry has been employed at this laboratory to obtain the accurate and precise temperature measurements required in bomb calorimetry. A novel technique of measuring temperature is now being tested. Through an arrangement initiated by F. D. Rossini* with DYMEC (A Division of Hewlett-Packard Co.), a demonstration quartz-crystal temperature measuring unit was placed in this laboratory for trial in high-precision calorimetric measurements.

The quartz crystal of the DYMEC temperature measuring unit has a new and unique angle of cut which provides a very linear, yet sensitive relation between the resonant frequency and the temperature of the crystal. The crystal is sealed in a probe and connected to a sensor oscillator. The frequency picked up by the sensor oscillator is heterodyned with a stabilized frequency from a reference oscillator. The frequency difference, which is a measure of the

* Consultant, University of Notre Dame, South Bend, Indiana.

temperature of the crystal, is fed to a counter which is designed to give directly, in degrees Centigrade, visual read-out and/or automatic print-out of the temperature. Measurements can be made to better than 0.0001°C .

The quartz-crystal thermometer was tested in two series of combustions of benzoic acid in oxygen. Temperatures were taken by manual recording of the visual read-out temperature at arbitrary intervals, and by automatic print-out of the time vs. temperature data. The precision of the results was comparable to that obtained with a platinum resistance thermometer. Measurement and recording of the data, however, were simplified considerably, particularly with the use of the automatic print-out system.

Figure IV-4

1500 $^{\circ}\text{C}$ DROP CALORIMETER

C. High Temperature Enthalpy Calorimetry

Two high-temperature enthalpy calorimeters of the drop type are being built: one for use up to 1500°C , and the other for use up to 2500°C .

1. 1500 $^{\circ}\text{C}$ Calorimeter

The 1500°C calorimeter unit (see Figure IV-4) consists of: a drop control mechanism by which the heated specimen may be dropped into the calorimeter and recovered for subsequent drops; a drop tube which rests on a furnace in which the sample is heated while suspended by a drop wire; a gate which is opened to drop the heated sample and is then closed around the drop wire; and a calorimeter where the heat evolved by the sample is measured. During the past year the system has been assembled and has been undergoing evaluation, with the results listed below:

(1) A regulated d-c power supply has been installed to provide current for the eddy current brake magnet of the drop mechanism. Acceleration and deceleration curves have been determined for the drop weight as a function of the trickle current in the brake magnet.

(2) Various drop wire materials were tested, including tantalum, National

Research Corp. "SGS" tantalum, tantalum-10% tungsten, molybdenum, tungsten-3% rhenium, and tungsten-25% rhenium. The most satisfactory wire found was pure tantalum.

(3) The present furnace consists of a tantalum-wound, four-element molybdenum core which is surrounded successively by a 100-mesh alumina grain dust shield, three molybdenum radiation shields and eight stainless steel shields; tantalum-sheathed thermocouples; and push-pull rods passing through the dust shield for alignment of the core. These modifications were made after expending much effort in testing and evaluating various materials and methods of operation of the furnace components.

(4) Temperature control of the furnace system is now operating satisfactorily. An optical viewing assembly, which consists essentially of a right-angle prism that can be moved into position below the gate, has been installed. With this arrangement, the primary furnace temperature can be measured directly by sighting a calibrated optical pyrometer on a floating shield. Alternatively, a thermocouple affixed to the floating shield and calibrated in place by means of optical pyrometer measurements can be used to measure the furnace temperature.

(5) The gate mechanism has been found to operate satisfactorily.

(6) The copper-block calorimeter proper (see ANL-6875, Figure IV-4, p. 132) has been calibrated under various operating conditions, e.g., with vacuum or inert gas in the interior space. The copper resistance thermometer of the calorimeter has been calibrated by comparison with a platinum resistance thermometer. Calculation from the raw data of the corrected temperature rise has been programmed for electronic computation.

The entire assembly is now being tested by measurements of the enthalpy of a sample of sapphire (Calorimetry Conference standard).

2. 2500°C Calorimeter

Figure IV-5 is a sketch of the 2500°C drop calorimeter system. Briefly, the system consists of a drop mechanism, a pressure chamber, a guide chamber, a motor assembly for rotating a cylindrical tantalum furnace core, two scanning electron guns for heating the furnace core, a calorimeter, a support stand for the entire system, and associated vacuum systems and control circuits. Most of the parts have been designed. Parts which have already been received include the electron guns and power supply, an adaptor plate which allows substitution of the copper-block calorimeter (same as used in the 1500°C calorimeter system) for an adiabatic calorimeter, and the support stand. Parts for the drop mechanism, the pressure chamber, the guide chamber, and the motor assembly are being constructed in the ANL Shops.

Figure IV-5

2500°C DROP CALORIMETER

Assembly of the 2500°C calorimeter system has only recently been reactivated.

V. REACTOR SAFETY

The program on reactor safety comprises three areas of research: (1) the study of metal-water reactions, (2) the study of the oxidation and ignition processes of substances used in reactor technology (this study is being curtailed to place greater emphasis on other portions of the program), and (3) recently initiated studies relating to the safety of fast reactors.

A. Metal-Water Reactions

The study of metal-water reactions is important because a large liberation of heat and hydrogen gas 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. It is possible that the energy released by such a reaction could exceed the energy released by the fission process during a nuclear excursion.

Current studies of metal-water reactions, as well as those in the past, can be divided into four categories. The first of these pertains to the experimental determination of isothermal rate laws and rate constants. These data are needed to develop mathematical expressions of reaction rates as a function of time and temperature for use in accident calculations. Isothermal studies also locate for a particular reaction, characteristic temperatures at which the nature of the reaction mechanism or products changes sharply. The second category covers nonisothermal studies of the reactions of small metal particles with water. Experiments are designed to simulate accidental situations under idealized conditions. The third category includes the in-pile studies in which simulation of reactor excursion accidents is more direct and in which the nature and degree of fragmentation of representative fuel element specimens are determined. In the fourth category are included calculational studies and accident analyses in which the experimental results from different methods are compared and methods of accident analysis devised.

1. Isothermal Reaction Rate Studies

a. Metal-Steam Reaction Studies by the High Pressure Furnace Method

Metals of primary concern in the safe operation of water-cooled reactors are uranium, zirconium, aluminum, and stainless steel. Enough isothermal data have been accumulated on uranium and zirconium reactions with steam to meet current needs in safety analyses. However, additional studies are required of the reactions of aluminum and stainless steel with steam. Previous isothermal studies were performed by induction or induction-levitation heating of metal samples in flowing steam (ANL-6875, p. 133 and ANL-6766, p. 100). The reaction of stainless steel with steam has been studied at tempera-

tures up to 1400°C. Above that temperature, the reaction rate increased sharply, owing to the disintegration of the metal to form an oxide foam. Sample disintegration and foaming resulted in a loss of coupling between the induction coil and the sample, thereby limiting useful studies to 1400°C and below. It became necessary, therefore, to develop a method of study that did not involve direct induction heating.

In addition to the need for high temperature isothermal studies of the stainless steel-steam reaction, there is a need for isothermal studies of the aluminum-steam reaction at elevated pressures, since results of in-pile studies have indicated that an increase in extent of aluminum-water reaction results from an increase in pressure (ANL-6875, p. 139). Although the isothermal reaction of aluminum with steam at one atmosphere pressure has been studied (ANL-6875, p. 133), laboratory studies have not been performed with steam at higher pressures.

A high pressure, high temperature furnace was constructed for the study of the reactions of stainless steel and aluminum with steam, and for a third usage, namely, the study of metal-steam reactions under conditions simulating those in a loss-of-coolant accident in a water-cooled reactor. In this type of accident, the cooling water is lost suddenly, through a break in the piping or in the reactor pressure vessel, and the reactor core self-heats from nuclear decay energy. The fuel elements in a typical power reactor will reach temperatures above 1000°C 5 to 10 min after a pipe break occurs. The fuel rods will be in a steam atmosphere at this time.

The preliminary design of the high pressure furnace was described in a previous report (ANL-6875, p. 135). The furnace, which is contained in a steel pressure vessel, consists of two zones, an internal steam-filled zone and an outer argon-filled zone. The outer zone contains molybdenum heater windings and zirconia insulation. The two zones are separated by an alumina tube; the pressures in the two zones are automatically matched to avoid stresses on the tube. The sample is loaded into the lower part of the inner steam-filled zone, which is maintained at about 800°C. To begin an experiment, the sample is raised into the upper part of the steam-filled zone by an external crank mechanism. It is expected that temperatures as high as 1700°C can be attained in the hottest part of the steam zone. Operating pressure is expected to be as high as 1000 psig.

A moderate flow of steam through the furnace is maintained. Effluent steam containing hydrogen produced by metal-steam reaction is condensed outside of the furnace. The hydrogen is collected continuously in order to determine the extent of metal-water reaction.

Initial experiments performed in the high pressure furnace were designed to simulate a loss-of-coolant accident. The samples used in the experiments, therefore, were sections of typical power reactor fuel elements.

Figure V-1

SIMULATED FUEL ELEMENTS BEFORE AND AFTER EXPOSURE TO STEAM
AT 1500°C AND 15 psig

A. 304 STAINLESS STEEL CLAD, UO₂ CORE

B. ZIRCALOY-2 CLAD, UO₂ CORE

One sample consisted of high density UO_2 pellets clad with type 304 stainless steel tubing 27 mils thick. The ends were welded to form a rod $3/8$ in. in dia. by 8 in. long. Another sample was identical with the first except that the cladding metal was Zircaloy-2. In the experiments the samples were raised into the hottest region of the furnace over a period of about 8 min and left there for 3 hr. While in the raised position, the upper end of the fuel elements reached a steady temperature of about 1500°C , whereas the lower ends reached only about 900°C . The steam pressure was maintained at 15 psig.

The two fuel samples after their exposure to steam are compared with unexposed samples in Figure V-1. The appearance of the exposed samples indicates a characteristic difference between the modes of failure of the two cladding metals. The stainless steel shows the formation of oxide foam. The oxide foam flowed downward, partially exposing the UO_2 pellets. The Zircaloy cladding, on the other hand, was converted into refractory ZrO_2 which remained relatively intact.

Hydrogen collected during the two experiments indicated that 62% of the stainless steel and 74% of the Zircaloy had reacted with steam. The quantity of hydrogen generated and the appearance of the samples both suggested that the upper (hottest) two-thirds of the sample fuel elements had reacted completely, but that the lower (cooler) one-third had not reacted significantly.

The principal result of these preliminary experiments is the demonstration of the mode of failure of the fuel elements. The samples were in contact with steam in the furnace longer than they would be in a loss-of-coolant accident and the quantity of steam available for reaction was greater in the furnace. Future experiments will be performed with a shorter exposure time. The results of these experiments can then be compared with calculated results. Computational methods are described in section V-A4 below.

b. Kinetics of Isothermal Reactions of Refractory Metals with Steam

A brief study of the kinetics of the isothermal reaction of refractory metals with steam was undertaken to determine the suitability of these metals as materials of construction for use in the high pressure furnace (described above) as well as to gain insight into the kinetics and mechanisms of high temperature metal-steam reactions. The metals studied included molybdenum, rhenium, tungsten, niobium, tantalum, zirconium, and also iron. While it was soon concluded that none of the metals was satisfactory for exposure to high temperature steam, the reactions have shown an interesting range of kinetic behavior.

In these experiments, a cylindrical metal sample containing an imbedded thermocouple was mounted on the end of a fine ceramic tube. The

sample, in an atmosphere of flowing steam, was heated rapidly to a constant temperature by an external induction coil. Reaction rate was followed by collecting evolved hydrogen in a eudiometer tube; the stoichiometry of the reaction was assessed by relating sample weight change to volume of hydrogen collected.

Figure V-2

COMPARISON OF THE LINEAR
VELOCITY CONSTANTS OF
MOLYBDENUM, RHENIUM, AND
TUNGSTEN

A linear rate law was observed for the reaction of steam with the metals that formed volatile oxides at the temperatures studied, namely, molybdenum, rhenium, and tungsten. Molybdenum, from 1100 to 1700°C; forms MoO_3 or $\text{MoO}_2(\text{OH})_2$ and polymeric oxides; rhenium, from 850 to 1700°C, forms Re_2O_7 ; tungsten, from 1000 to 1700°C, forms WO_3 or $\text{WO}_2(\text{OH})_2$ and probably polymeric oxides. Linear rate constants for these three metals are plotted as a function of reciprocal absolute temperature in Figure V-2. The change in the reaction rate of tungsten at about 1400°C suggests a change in the reaction mechanism at this temperature.

In the reaction of steam with molybdenum, a slight tarnish immediately developed on the surface of the molybdenum and was retained throughout the reaction. This suggests that the reaction proceeded through the formation of a nonvolatile intermediate, MoO_2 . Rhenium remained bright throughout the reaction; however, many small, randomly oriented crystals of metal formed on the surface. With tungsten, a thin oxide film developed on the surface of the metal as the reaction was initiated. For reaction at about 1200°C, the oxide material was identified as WO_2 and $\text{W}_{20}\text{O}_{58}$. For reaction at temperatures above 1500°C, the surface film contained $\text{W}_{18}\text{O}_{49}$. The initial reaction with polished tungsten was very rapid and resulted in

momentary self-heating while the surface coating was built up. The linear reaction proceeded smoothly after the development of the film. When samples

were used which were already covered by an oxide film, the initial rapid reaction and self-heating were not observed.

A parabolic rate law was observed initially for the reaction of steam with metals forming nonvolatile oxides, namely, tantalum, niobium, and zirconium. In some cases the rate of reaction became linear after a period of time. Initial parabolic oxidation in steam followed by linear oxidation occurred with tantalum over the range 950-1300°C. The oxide product formed below 1200°C was β -Ta₂O₅; at higher temperatures α -Ta₂O₅ was found. Above 1300°C the rate of reaction became too fast for measurement. The reaction rate of niobium over the range 1050-1500°C appeared initially to be between linear and parabolic but became linear within a few minutes. Only β -Nb₂O₅ could be identified in the oxide coating; however, it is likely that there were sublayers of NbO or NbO₂. Reaction kinetics for zirconium over the range 1100 to 1700°C could be described precisely by a parabolic rate law; this is in agreement with previous results obtained by other methods (see ANL-6548).

The reaction of iron with steam followed a parabolic rate law over the range 950-1300°C. The weight gain of the sample showed the overall composition of the resulting oxide film to be FeO_{1.14}. This stoichiometry suggests that wustite, FeO, is the principal product, but that some higher oxides are also formed. Above the melting point of wustite, 1370°C, oxide frothing and a greatly increased rate of oxidation took place. The reaction rate of type 304 stainless steel with steam was parabolic up to about 1400°C; however, the rate was an order of magnitude lower than that of pure iron. Oxide melting and frothing, and the resulting increase in reaction rate, also occurred with stainless steel at about 1400°C. These experiments showed that pure iron underwent a foaming process similar to that reported earlier (Section V Ala) for stainless steel.

2. Nonisothermal Reaction Studies

The nonisothermal studies were undertaken to study the reaction of the metals of interest in the form of fine particles with rapidly changing temperatures. The experiments were designed to discover particular aspects of the reaction that might be peculiar to fine particles. Fine particles of molten metal are likely to be produced in reactor accidents where there is a violent meltdown of the reactor core. Initially, the method of studying nonisothermal metal-water reactions in this program was the condenser discharge method. In these studies, wires of zirconium (ANL-6548), uranium (ANL-6183, p. 141), and stainless steel (ANL-6766, p. 99) were heated, almost instantaneously, in a water environment by a surge current from a bank of condensers. A large number of particles were formed as the wires melted. More recently, a method was devised in which the behavior of a single molten particle could be observed. The use of a single particle removes the uncertainties resulting from the differing behaviors of a variety of particles having a range of sizes.

The laser method has been applied principally to studies of the aluminum-water reaction because aluminum could not be heated satisfactorily by the condenser discharge method. In the laser method, a small square of aluminum foil is heated and melted by the energy of a light beam from a ruby laser. Preliminary results by the laser method were given in a previous report (see ANL-6875, p. 138).

A series of laser experiments were performed with small aluminum foil specimens (1 by 1 by 0.025mm). The experiments were carried out by submerging the small specimen of aluminum foil under water in a fused silica cell. The aluminum sample was located just above an optically flat cell window. The cell was sealed off under vacuum after the water had been degassed. The cell was then arranged so that a focussed laser beam would impinge uniformly across one face of the specimen. The laser beam typically persists for about 0.001 sec. Following exposure, the minute quantity of hydrogen produced by metal-water reaction is measured and the extent of reaction computed from the analytical result.

Figure V-3

EXTENT OF ALUMINUM-WATER REACTION IN LASER HEATING
EXPERIMENTS CONDUCTED IN 25°C WATER

Nominal particle diameter: 360μ

In the series of experiments with small aluminum foils, the specimens were submerged in water at 25°C or at 100°C (overpressure of 1 atm of steam). The foils were exposed to laser beams of varied energies. In each experiment the foil was converted to a single sphere with a diameter of about 360 μ . The extent of metal-water reaction is plotted as a function of the energy of the laser beam in Figure V-3 for experiments conducted in 25°C water and in Figure V-4 for experiments conducted in 100°C water. The extent of reaction in room temperature water varied from 6 to 11% and was independent of laser energy in the range 10 to 49 joules. In 100°C water, there was no reaction up to a critical energy of about 40 joules. At laser beam energies above 45 joules, reaction was substantially complete. The particles produced in three runs in 100°C water are shown in Figure V-5. The appearance of the particle in Figure V-5b (13% reaction) produced in the 40-45 joule transition region, is very similar to that of particles heated in 25°C water. The particle shown in Figure V-5c, which had reacted completely, was a nearly transparent ball of Al₂O₃. Its appearance suggests that it was formed in a molten state.

Figure V-4

EXTENT OF ALUMINUM-WATER REACTION IN LASER HEATING
EXPERIMENTS CONDUCTED IN 100°C WATER

Nominal particle diameter: 360 μ

Figure V-5

APPEARANCE OF ALUMINUM PARTICLES AFTER TRANSIENT LASER BEAM HEATING IN WATER

Nominal particle diameter: 360μ

Water Temperature: 100°C

	<u>Laser Output Energy (Joules)</u>	<u>Percent Reaction</u>
a.	39	0
b.	44	13
c.	46	97

a

b

c

100μ
┌───┐

The interpretation of the laser studies of the aluminum-water reaction has been aided by recent findings of a number of other investigators who have studied the aluminum-oxygen reaction. It has been reported that small aluminum particles do not ignite in oxygen-containing burner flames until the aluminum reaches the melting point of Al_2O_3 (2050°C).¹ It is hypothesized that when the oxide film melts, its protectiveness is lost and an ignition occurs. The sharp energy threshold for reaction in 100°C water and the appearance of the oxide residue suggest that a similar phenomenon occurs in this medium. In 25°C water, it appears that a different process occurs because of the lower pressure of the system. At lower total pressure, the vapor pressure of aluminum would exceed the ambient pressure at temperatures below the oxide melting point. The protectiveness of the oxide film might then be lost as a result of a pressure differential rather than as a result of oxide

¹ Friedman, R., and A. Macek, Ignition and Combustion of Aluminum Particles in Hot Ambient Gases, Combustion and Flame, 6, 9 (1962).

melting. The metal temperature would not reach the oxide melting point; metal vaporization would occur instead.

The effect of particle size on the aluminum-water reaction was also studied by the laser method. In general, it was found that the extent of reaction in 25°C water increased with decreasing particle size. With particles having equivalent sphere diameters greater than about 500 μ , the phenomenon of particle breakup was observed.

Current studies are being performed with a reaction cell constructed of stainless steel. These studies will extend the range of pressure to 10 atm.

The results of the laser experiments have shown that the reaction of small aluminum particles in water is considerably different from that of larger aluminum specimens in steam. Additional studies by the furnace method and by the laser method are required before the reaction mechanism can be satisfactorily understood.

3. In-Pile Studies

The reactions of specimens of typical reactor fuel in a water environment are being studied by subjecting the fuel to a burst of neutrons in the Transient REActor Test facility (TREAT). The recent Kiwi-TNT destructive transient in Nevada also provided an opportunity for several short period experiments. These in-pile experiments are intended to provide a more direct simulation of the conditions prevailing during a nuclear excursion in a water-cooled reactor.

In the in-pile experiments, a stainless steel autoclave contains the specimen and the water. Extent of metal-water reaction is determined by measuring the quantity of hydrogen evolved. Subsequently, particle sizes are determined and metallographic studies are made.

The status of the in-pile studies is indicated in Table V-1. Experiments in TREAT with uranium metal and uranium-rich metallic alloys have been completed. The first experiments were performed with single pins and wires of uranium in 25°C water with a 20 psia helium overpressure. Experiments were then performed to determine the effects of: (a) heated water (285°C, 1000 psia), (b) preirradiation of the uranium to 0.3% total atom burnup, and (c) clustering of nine 5 5/8-in. long fuel pins. The results for the extents of reaction are plotted in Figure V-6 and indicate that the water temperature (and resultant vapor pressure) was the only variable that significantly affected the extent of reaction.

The performance of the scale-up (cluster) experiments in which nine fuel pins were irradiated simultaneously represented a significant achievement in the field of transient in-pile experimentation. The quantity of

Table V-1

STATUS OF IN-PILE STUDIES

<u>Fuel Type</u>	<u>Room-Temp. Water^a (20 psia He)</u>	<u>Heated Water^a 285°C (1000 psia)</u>	<u>Preirradiated Fuel^a</u>	<u>Photographic Experiments^a</u>	<u>Large-Scale Fuel Clusters^a</u>	<u>Short Period^b</u>
<u>Metallic</u>						
Uranium metal (including uranium- rich alloys)	Completed	Completed	Completed	---	2 Runs	6 Runs
Aluminum-rich uranium alloys	Completed	Completed	2 Runs	Experiments in Preparation	---	6 Runs
Zirconium-rich uranium alloys	Completed	3 Runs	Samples Preirradiated	---	---	---
<u>Cermet</u>						
Aluminum-U ₃ O ₈	4 Runs	---	---	---	---	---
Stainless steel-UO ₂	Completed	---	---	---	---	---
<u>Oxide (UO₂ or Mixed Oxide Core)</u>						
Aluminum-clad	Completed	---	---	---	---	---
Zirconium-clad	Completed	---	Samples Preirradiated	---	Samples Prepared	6 Runs
Stainless steel-clad	Completed	---	Samples Preirradiated	---	Samples Prepared	6 Runs

^a In TREAT.^b Kiwi-TNT Test, Mercury, Nevada, Jan. 12, 1965.

Figure V-6

EXTENT OF METAL-WATER REACTION OBSERVED IN TREAT EXPERIMENTS WITH URANIUM AND URANIUM-RICH FUEL SAMPLES

Reactor periods of 63 to 515 msec

enriched uranium contained in the nine-pin cluster was a factor of 100 greater than that contained in the single pin experiments. A digram of the autoclave used in the scale-up experiments is shown in Figure V-7. The original fuel pin cluster is compared in Figure V-8 with the appearance of the residue collected from the autoclave following the two scale-up experiments.

Scale-up experiments will be performed with stainless steel-clad and Zircaloy-clad UO₂ fuel pins in the near future. Development of apparatus for taking high speed motion pictures of TREAT experiments is being pursued. Initial efforts in the photography experiments will be concentrated on aluminum-rich uranium alloys because of the apparent complexity of the aluminum-water reaction exhibited in previous TREAT experiments.

Figure V-7

CAPSULE FOR 9-PIN CLUSTER
URANIUM-WATER EXPERIMENTS
IN TREAT

The TREAT results are proving valuable in providing a guide to the factors which influence the extent of metal-water reaction during a nuclear excursion. It was shown previously (ANL-6875, p. 144) how TREAT results with aluminum-uranium alloy fuel could be applied to predict the extent of reaction occurring in actual reactor meltdown incidents. Although no reactor incidents have occurred with other types of fuel material, analyses of the consequences of hypothetical accidents can now be performed with greater reliability.

In TREAT, reactor periods are limited to a minimum of about 40 msec. The period is the time for the reactor power to increase by a factor of e (2.718). Because periods of the order of a few msec have occurred in destructive nuclear excursions, it is evident that information on metal-water reactions at very short periods is of considerable importance. We were particularly fortunate, therefore, in being able to participate in the Kiwi-TNT test conducted in Nevada on Jan. 12, 1965. In this experiment a nuclear rocket reactor was intentionally programmed for an excursion with a period of less than 1 msec. As a result of the test, the reactor was completely destroyed. Prior to the test, 24 small autoclaves had been located at distances of from 1 to 12 ft from the periphery of the reactor; each autoclave contained a fuel specimen immersed in water. The type of fuel specimens and the number tested are indicated in Table V-1. Twenty-three of the autoclaves were recovered following the transient and have been returned to ANL. Post-irradiation observations and analyses of the fuel samples are now being made.

Figure V-8

APPEARANCE OF ENRICHED URANIUM FUEL ROD CLUSTER BEFORE
AND AFTER SCALE-UP EXPERIMENTS IN TREAT

- a. Fuel Rod Cluster Before Irradiation.
- b. Fuel Rod Cluster After Irradiation in Experiment CEN-196S (124 cal/g).
- c. Fuel Rod Cluster After Irradiation in Experiment CEN-197S (302 cal/g).

a

b

c

It is expected that analyses of the hydrogen generated by metal-water reaction will provide information on extent of reaction which can be compared with similar data gathered in TREAT experiments. Examination of the damage to fuel specimens will disclose any effect of reactor period not known heretofore.

4. Calculational Studies

Calculational studies include mathematical comparison of experimental results obtained from different methods and the development of techniques for accident analysis. Two major efforts were undertaken in the area of accident analysis. One of these efforts was directed toward quantitatively predicting the transient pressures generated by transient boiling during a nuclear excursion. The other was the application of metal-water reaction data to the analysis of a loss-of-coolant accident in a water-cooled power reactor.

The first calculation study was made to gain an understanding of the violent pressure surge produced during the deliberate meltdown of the SPERT-1 reactor. In the SPERT (Special Power Excursion Reactor Test) experiment, a power excursion with a 3.2-msec period was initiated. About 15 msec after peak

power, an explosion occurred which produced pressures in excess of 3000 psia at the center of the reactor and lifted some of the water in the open reactor tank to a height of 90 ft.

Figure V-9

COMPUTED PRESSURE-TIME CURVES FOR DESTRUCTIVE (SECOND) PRESSURE PULSE IN SPERT-1D REACTOR EXPERIMENT

In the transient pressure calculations, it was assumed that the explosive pressure rise began as the molten fuel plates at the center of the reactor started to break up. It was also assumed that the heat transfer rate was controlled by thermal conduction across a growing steam film. An energy balance equation was developed which included the heat transfer rate. Another equation was developed to describe the acoustic constraint imposed by the large column of water above the relatively small reactor core. These equations were programmed on the CDC-3600 digital computer and were solved using several assumptions concerning the nature of core breakup and the quantity of compressible gas within the core at the time of the destructive pressure surge.

Computed pressure-time curves for three values of the increase of surface area resulting from core breakup and for three values of compressible gas content are given in Figure V-9. The results indicated that a 3000-4000 psi pressure rise could result from rapid steam generation. The fact that the reactor was shut down at the time of the explosion implied that there was considerable steam present, i.e., enough to shut the reactor down because of moderator loss. This steam would presumably act as compressible gas and cushion the explosion. It appears from the results of the calculations that the assumption of thermal conduction heat transfer gives low heat transfer rates. Future refinement of the calculational model will depend upon experimental determinations of heat transfer rates under conditions prevailing in the reactor.

The second major calculational effort was an application of metal-water reaction data to the analysis of a low-of-coolant accident in a water-cooled power reactor. The reactor conceived for the LOFT (Loss of Fluid Test) facility² was used as a model with the assumption that the cylindrical UO_2 -core fuel pins were clad with 25-mil thick zirconium. In the proposed accident, the core temperature rises because of decay heating, after a 10-sec blowdown which completely uncovers the reactor core. The core eventually collapses owing to melting of the cladding.

In this study the temperature and the extent of cladding-steam reaction for the core were calculated as a function of time. To facilitate these calculations, the core was divided into ten sections represented by various rates of decay heating. The calculations were performed for each section by numerically solving two differential equations on an IBM-704 computer. The rate of reaction of zirconium with steam, when the reaction was not limited by the quantity of steam, was described by a parabolic oxidation law (see ANL-6548). When the reaction was limited by the steam flow through the core, the reaction rate was assumed to be equal to a constant calculated by dividing the mass steam flow rate by the total cladding surface area. An energy balance, in which the energy accumulation in the fuel and cladding was equated to the chemical energy and decay energy developed in them, was used to calculate the temperature-time history of individual sections of fuel rod. Heat losses were ignored. Several other simplifying assumptions were made, namely, that the decay energy was distributed in the same manner as the reactor power, that the temperature of the cladding was equal to that of the fuel at any point along individual fuel rods, and that the heating and reaction of support structures could be ignored.

Calculations were performed for four cases according to the availability of steam to the core: (1) unlimited steam flow, (2) a steady flow rate

² Wilson, T. R. et al, An Engineering Test Program to Investigate a Loss-of-Coolant Accident, Report IDO-17049, Phillips Petroleum Co., October 1964.

4

of 1000 pounds of steam per hour through the core, (3) a steady flow rate of 100 pounds of steam per hour through the core, and (4) no steam flow, i.e., no metal-steam reaction. With an unlimited quantity of steam available the cladding begins to react in each section when the temperature reaches about 800°C. At the time of melting of the cladding about 5 mils of the cladding (20%) has reacted, but the rate of reaction is so rapid that ignition occurs and the reaction goes rapidly to completion. In the steam-limiting cases (1000 and 100 lb/hr) the temperature rises less rapidly. In the case of 1000 lb/hr flow, the reaction is steam-limited after the temperature in each section reaches about 1250°C and in the case of 100 lb/hr, the reaction is similarly limited at about 900°C.

Table V-2

TIME REQUIRED FOR COLLAPSE OF CORE AFTER BLOWDOWN AND
EXTENT OF REACTION BASED ON THE AVERAGE NUCLEAR DECAY AND
CHEMICAL ENERGY CONTENT

Steam Flow	Case of Average Core Energy Sufficient to Melt Metal Cladding Completely (1852°C)		Case of Average Core Energy Sufficient to Begin to Melt Fuel (2800°C)	
	Collapse Time (sec)	Percent Metal Reacted	Collapse Time (sec)	Percent Metal Reacted
Unlimited	465	40	765	62
1000 lb/hr	740	21.0	1080	41
100 lb/hr	1200	6.0	2090	13
No flow (No metal-water reaction)	1400	none	2600	none

In order to compare the results of the calculations, a simple core melt-down model was used. The core was assumed to collapse when the average energy in the core, accumulated from the nuclear decay and chemical reaction, was sufficient to melt the fuel rods (either the zirconium cladding, 1852°C, or the uranium fuel, 2800°C, in the case of extensive cladding oxidation). The core collapse times and the extents of cladding reaction at these times are tabulated in Table V-2 where the effects of the zirconium-steam reaction on the core behavior are apparent.

The results of the calculational studies are being used by reactor

designers in evaluating the quantity of chemical energy and hydrogen gas that must be safely dissipated within reactor buildings.

B. Metal-Oxidation and Ignition

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

A study was made of the ignition of preirradiated uranium to determine the effect of irradiation on ignition behavior. The uranium samples were 20% enriched pins (0.2-in. dia. by 0.25-in. long). The samples were enclosed tightly in tantalum-lined, stainless steel jackets during irradiation in the Materials Testing Reactor. The constraintment jacket assembly and the irradiation capsule are shown in Figure V-10. The constraintment jackets were employed to minimize surface roughening, directional growth, and swelling of the samples during irradiation.

Figure V-10

STAINLESS STEEL CAPSULE AND JACKET ASSEMBLY FOR MTR IRRADIATION OF URANIUM IGNITION SAMPLES

Four groups of samples were used. One group of samples was irradiated to 1.71% burnup of the uranium-235 present; another group was irradiated to 0.79% burnup. The other two groups of samples were unirradiated. Of the unirradiated samples, one group was subjected to a pattern of thermocycling similar to the thermocycling of the irradiated samples; the other group remained untreated and were used as controls.

An ignition apparatus was constructed which could be operated remotely in the Senior Cave Facility. The ignition test employed is one in which samples are heated in a flowing oxidizing atmosphere (either air or oxygen) at a uniform rate of $10^{\circ}\text{C}/\text{min}$. The sample first self-heats beyond the furnace temperature and then may ignite. Ignition temperature is determined graphically as the point of intersection between the pre-ignition heating rate and the post-ignition self-heating rate. The sample temperature-time curve is called a burning curve. For tests in pure oxygen, temperatures were measured by a thermocouple which

Figure V-11

TEMPERATURE-TIME TRACES (BURNING CURVES) OF 20% ENRICHED URANIUM SAMPLES HEATED IN FLOWING OXYGEN.

Furnace heated at $10^{\circ}\text{C}/\text{min}$.

Ignition temp. determined by graphical method as indicated

was in contact with the sample. For experiments in air, it was necessary to drill small holes in the samples and imbed the thermocouple within the samples in order to record the temperatures accurately.

Typical burning curves are shown in Figure V-11 for oxygen and in Figure V-12 for air. It is apparent that preirradiation markedly reduced the ignition temperature of uranium in oxygen. The behavior of the control samples was identical with that of thermocycled, but unirradiated, samples. Burning curves obtained in air did not show well-defined ignitions; however, greater self-heating of the irradiated samples compared with control samples occurred at about 450°C.

Figure V-12

TEMPERATURE-TIME TRACES (BURNING CURVES) OF 20% ENRICHED URANIUM SAMPLES HEATED IN FLOWING AIR

Furnace heated at 10°C/min.

Thermocouple embedded in drilled specimens

The reactivity increase caused by irradiation may have been due, in part, to surface roughening which occurred in spite of the constraint imposed on the samples during irradiation. Another possible cause of the increase in reactivity is interference of the protective oxide film by the presence of fission products.

From the data, one must conclude that the ignition hazard for irradiated uranium is somewhat greater than that for unirradiated uranium.

C. Fast Reactor Safety Studies

A program of research has been initiated in which knowledge gained during studies of metal-water reactions will be applied to certain potential problems in fast reactor safety. Four problem areas are being studied.

1. Survey Study of the Chemical Interactions of Molten Sodium at High Temperatures with Fuel and Cladding Materials

This study will develop information, now lacking, on the nature of the interaction of molten sodium at high temperatures with fuel and cladding materials, such as molten uranium, plutonium, stainless steel, titanium, and vanadium; solid uranium and plutonium oxides and carbides; and other potential fast reactor fuels, such as uranium nitrides and sulfides. Of particular interest are the problems associated with loss of integrity of cladding and subsequent behavior of the fuel. The studies would be carried out first on unirradiated fuel pieces, then later on highly irradiated fuel.

The method to be used in the initial effort involves the levitation and melting of pellets of cladding metals in a radiofrequency field, and subsequent dropping of the hot molten pellets into molten sodium. Nonmetallic materials will be heated by induction (using a graphite susceptor) and dropped mechanically. The residues will be filtered from the sodium and examined for chemical and physical changes. It is probable that calorimetric measurements can be carried out in the event that an exothermic interaction takes place. Further studies will hinge on the results of the initial investigation.

The apparatus designed to heat the pellets has been constructed and installed in a glovebox which will contain an argon atmosphere as shown in Figure V-13. The apparatus is complete and a number of samples have been procured. Experiments will begin when installation of the argon purification system for the glovebox has been completed.

2. Fuel Migration and Segregation in Mixed Uranium-Plutonium Compounds

Studies of fuel migration and segregation in mixed uranium-plutonium compounds are to be undertaken. Segregation of the uranium and plutonium compounds within the fuel may seriously decrease the effectiveness of Doppler

Figure V-13

GLOVEBOX FOR STUDIES OF INTERACTION OF MOLTEN FUEL AND
CLADDING MATERIALS WITH MOLTEN SODIUM

Glovebox to contain purified argon atmosphere

broadening as a shutdown mechanism in a nuclear reactor, since more time will be required before heat generated within the plutonium can be transferred to the uranium. Experiments are planned in which the degree of segregation will be measured in typical uranium-plutonium mixed fuels.

In the initial experiments, small pellets of typical mixed fuels will be heated for extended periods of time in a furnace designed to impose a sharp temperature gradient across one dimension of the sample. Samples will then be cut into wafers and concentration gradients induced by the temperature gradient will be determined by chemical analysis of individual wafers. An experimental furnace has been constructed and is presently being tested to determine the extent of the temperature gradient that can be developed across small pellets of mixed fuel.

3. Transient Boiling of Molten Sodium

It is planned to examine the qualitative and quantitative aspects of explosive (nonchemical) generation of vapor which may occur on contact of melted fuel with sodium. It is believed that this will be a more violent occurrence than that of molten metal with water under similar conditions. It is expected that these studies will lead to means of calculating explosive pressures developed during meltdown accidents. The laboratory experiments will be followed by in-pile meltdown tests in TREAT.

Initial experiments are being undertaken with water in place of sodium, not only to develop the methods but also to obtain needed data on transient boiling in water. Four experimental procedures are under development.

4. Determination of High Temperature Physical Properties of Fast Reactor Materials

This program is directed toward developing methods for the measurement of physical properties at high temperatures. Data on properties such as specific heat, thermal conductivity, and density are needed for application to fast reactor accident models. Studies are underway to determine which property measurements are needed for uranium carbide and uranium nitride fuels. It is anticipated that the measurement procedures will be needed for materials produced by new production methods currently under development by other research groups at ANL. Special attention will be given to studies of compounds or physical states produced by interactions between fuel, cladding, and coolant. Future studies will also include effects of irradiation on physical properties of fuels.

VI. ENERGY CONVERSION

A regenerative emf cell operating in a closed cycle to convert heat to electricity is an attractive energy conversion device. The studies being undertaken at Argonne are concerned with devising regenerative cell systems which can be coupled eventually to a reactor heat source. The principal advantages of these systems are the elimination of most of the moving parts that are found in conventional systems, compactness (a low weight per unit of power output), and a long, maintenance-free life. The applications of such systems might be for remote terrestrial and extraterrestrial power units, energy depots for armed services, and propulsion units for ships and large vehicles.

A. Regenerative Emf Cells -- Physical-Chemical Laboratory Studies

Regenerative emf cells would operate continuously in a closed Carnot cycle, subject to Carnot efficiency limits for the overall conversion of heat to useful energy. An emf cell would function in one isothermal leg of a Carnot cycle; regeneration of the cell products could be accomplished by thermally dissociating the products of the cell reaction or by operating a second cell in the high temperature isothermal leg of the Carnot cycle. The initial work has been concentrated on the spontaneous thermal regeneration of the cell products in the systems currently under consideration. This type of regeneration requires the physical separation at high temperature of the anode and cathode reactants. These considerations have led to the study of two types of emf cells for possible application in a regenerative cycle. These are the hydride cell and the bimetallic concentration cells.

The hydride cell consists of an anode of molten metal, an electrolyte of molten salts containing the anode metal ion, and a hydrogen gas cathode. In cell operation, the liquid anode metal is oxidized to ions of the metal and the hydrogen gas is reduced to hydride ions. At the present time, only lithium hydride is of practical interest for application in a regenerative hydride cell.

The bimetallic cells have two liquid metal electrodes in contact with a molten salt electrolyte which contains only the salts of the anode metal. The anode metals under consideration are lithium and sodium. The overall cell reaction is the oxidation of the metallic anode to produce metal ions in the electrolyte, and the reduction of the metal ions in the electrolyte at the cathode to produce an alloy.

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

studied include lithium-bismuth, lithium-tin, and sodium-bismuth. The lithium-bismuth bimetallic cell system has been previously reported (ANL-6875, p. 151).

1. Bimetallic Cell Studies: Lithium-Tin

Electromotive force measurements have been made on lithium-tin concentration cells (see ANL-6875, p. 152) without transference for temperatures between 500 and 700°C. A purified eutectic mixture of 70 m/o LiCl-30 m/o LiF was the electrolyte.

The phase diagram of the lithium-tin system as given by Hansen and Anderko¹ shows that for alloy compositions between pure tin and 30 a/o tin in lithium and between temperatures of 502 and 720°C, either a one phase liquid alloy or a liquid alloy of tin saturated with Li₅Sn₂ (solid) exists.

Initial voltage measurements were made with a cell of Type 1:

This cathode alloy (overall composition 30 a/o Sn) would be analogous to the reference electrode of Bi (l) saturated with Li₃Bi (s) (overall composition 40 a/o Bi) that had been used in previous experiments.² The voltages measured for a cell of Type 1 were reasonably steady at constant temperature, but responded slowly to temperature changes. The cell was modified to one of Type 2:

However, the response of voltage to temperature changes for this cell was slower than that of the Type-1 cell.

In order to solve this problem, a secondary reference electrode, which consisted of liquid bismuth saturated with Li₃Bi (s) (overall composition 40 a/o bismuth), was substituted for the alloy of 30 a/o tin in lithium. Its potential was previously measured independently against the pure lithium electrode. The validity of the use of this reference electrode was established by measuring its potential against an electrode of liquid tin saturated with Li₅Sn₂ (s) and by spot checking with a pure lithium electrode.

¹ Hansen, M., and K. Anderko, Constitution of Binary Alloys, McGraw-Hill Book Co., New York, N. Y., 1958, p. 904.

² Foster, M.S., S.E. Wood, and C.E. Crouthamel, J. Inorg. Chem. 3, 1428 (1964).

Since the reference electrode substitution proved feasible, cells of Type 3:

were set up with $x_{\text{Li}} = 10, 20, 30, 40$, and 50 and were operated without incident.

Data from cells of Types 2 and 3 were combined with the appropriate reference electrode data to yield data applicable to a cell of Type 4:

The emf-temperature characteristics of a cell of Type 4 are shown in Figure VI-1 where curves are plotted for data obtained using the Li-Bi

Figure VI-1

VOLTAGE-TEMPERATURE-
COMPOSITION DATA OF THE CELL

$\text{Li (l)} / \text{LiCl-LiF} / \text{Li in Sn}$
 $x_{\text{Li}} = \text{atom percent lithium}$
 $\sigma = \text{standard deviation of points from curve}$

reference electrode and a pure Li anode. The curve for Sn (l) sat'd with Li_5Sn_2 shown in the figure was previously reported (ANL-6875, p. 154) and is included for comparison.

A mathematical analysis of the data is now in progress.

2. Intermetallic Compounds and Alkali Metal in Fused Salts

In the operation of a bimetallic concentration cell, the solubilities of both the alkali metal (from the anode) and the intermetallic species (from the cathode) in the fused salt electrolyte give rise to an irreversible transfer of material between electrodes. The irreversible transfer of alkali metal from the anode to the cathode may be overcome by an increased rate of regeneration. However, the irreversible transfer of cathode material to the anode, if appreciable, must be dealt with by other schemes. The rates of these irreversible transfers are expected to be proportional to the solubilities of the species in the electrolyte. Thus, it is of interest from the standpoint of cell operation to determine the solubilities of alkali metal

and intermetallic species in the electrolyte.

a. Solubility of Li_2Te in Molten Salt Solvents

In an effort to determine the nature and scope of the phenomena involved in the solubility of intermetallic compounds in molten salt solutions, the investigation of several types of compounds was begun, starting with probably the most ionic compounds - the alkali metal tellurides, M_2Te , where M is an alkali metal.

The solubility of Li_2Te in certain fused salt solvents has been determined and is shown in Figure VI-2. The fused salts were saturated with

Figure VI-2

RELATIVE SOLUBILITIES OF Li_2Te AND Li_3Bi IN MOLTEN SALT SOLVENTS

Li_2Te at various temperatures. The following values were obtained for the solubility: (1) in 70 m/o LiCl -30 m/o LiF at $\sim 525^\circ\text{C}$, 2.62 moles/liter; (2) in 59 m/o LiCl -41 m/o KCl at $\sim 400^\circ\text{C}$, 0.57 mole/liter; (3) in CsCl at $\sim 700^\circ\text{C}$, 8.9 moles/liter. These values were calculated from results of tellurium analyses by permanganate titration, assuming that the species present was Li_2Te . For comparison, the solubility of Li_3Bi in a LiCl - LiF (70 m/o LiCl) solvent at temperatures between 675 and 1000°C (see ANL-6875, p. 156) has also been plotted in Figure VI-2. The solubility of Li_2Te is two orders of magnitude larger than that of Li_3Bi .

b. Solubility of Li-Bi Intermetallic Compounds in LiCl - LiF

At temperatures between 505 and 610°C , the system with an overall composition of 50 a/o lithium in bismuth consists of a solid Li_3Bi phase and a liquid bismuth-rich phase saturated with Li_3Bi (s). Above 610°C , the bimetallic system exists as a single liquid phase. Therefore, the solubility of lithium and bismuth in a fused salt above a 50 a/o lithium-bismuth alloy would be expected to be

the same as that of Li_3Bi (s) at temperatures between 505 and 610°C , and to be lower than the solubility of Li_3Bi at higher temperatures.

The solubility of lithium and bismuth from a 50 a/o lithium-bismuth

alloy in LiCl-LiF eutectic has been measured. The bismuth content was determined by a complexometric titration, and the lithium content by a hydrogen evolution-gas chromatographic technique. The results for the bismuth species are shown in Figure VI-3, and are compared with those previously obtained (ANL-6875, p. 156) for a 70 a/o lithium-bismuth system.

Figure VI-3

SOLUBILITY OF BISMUTH FROM
Li-Bi ALLOYS (X_{Li} = atom fraction lithium) IN
LiCl-LiF

c. Solubility of Na_3Bi and Na in
NaI-NaCl-NaF Eutectic

In the sodium-bismuth bimetallic concentration cell, sodium metal and Na_3Bi are the species of interest in the determination of solubilities of various species in the electrolyte. The electrolyte which has been selected for use in the sodium-bismuth bimetallic concentration cell is the ternary eutectic 53.2 m/o NaI-31.6 m/o NaCl-15.2 m/o NaF. It has a melting point of 530°C, one of the lowest found in any of the sodium halide ternary systems.

Two experiments were made to determine the solubility of sodium in the ternary mixture NaI-NaCl-NaF. In both experiments, the electrolyte, in contact with molten sodium, was held at a given temperature until equilibrium was established. Samples of the electrolyte were taken with tantalum sampling buckets through a tantalum tube immersed in the molten salt. Results of these experiments

are shown in Figure VI-4. Values for the solubility of sodium in the electrolyte range from 0.3 m/o at 546°C to 0.9 m/o at 697°C. The scatter of the points is somewhat higher than desired; however, since the data show that reasonable temperature agreement and proper temperature dependence were achieved, the points are believed to indicate true solubility and not dispersions or colloidal solutions. Note that the value given by the one datum point for the binary eutectic mixture 63.6 m/o NaI-36.7 m/o NaCl, which was a trial electrolyte, shows essentially the same solubility as for the ternary eutectic mixture at 630°C. This agreement would be expected since NaI and NaCl are the major components of the ternary eutectic.

The solubility of solid Na_3Bi in the ternary eutectic mixture of NaI,

Figure VI-4

SOLUBILITY OF SODIUM IN
MOLTEN SALT SOLVENTS

Figure VI-5

SOLUBILITY OF Na_3Bi IN
EUTECTIC MIXTURE
OF NaI-NaCl-NaF

NaCl, and NaF has also been studied. Samples of the melt, in equilibrium with Na_3Bi , were taken using a technique in which the samples were filtered through a tantalum frit. The samples were dissolved in water, filtered to separate the black bismuth metal precipitate, and the solution titrated with standard acid to determine sodium as the hydroxide. The bismuth was dissolved in nitric acid and titrated complexometrically.

The results of the Na_3Bi solubility experiments are shown in Figure VI-5. Values for the solubility of Na_3Bi in the ternary eutectic ranged from 1.2 m/o at 552°C to 8.5 m/o at 839°C. The average Na:Bi atom ratios were 2.98 ± 0.03 and 2.95 ± 0.03 for experiments 3 and 4, respectively (excluding the two points shown above the compound melting point at 839°C, for which the average ratio was 2.77 ± 0.03). In further experiments, the solubility of intermetallic sodium-bismuth alloys which are not of stoichiometric composition will be studied. These will correspond more closely to anticipated cell operating conditions where no solid phase is present in the cathode alloy.

Although the solubilities of both sodium and Na_3Bi will result in irreversible transfer, it is anticipated that the rates of transfer can be minimized by proper selection of cell operating variables and cell components.

d. Cryoscopic and Solid-Liquid Equilibrium Studies of Intermetallic Compounds and Fused Salts

Thermal analysis experiments have been initiated to study the solid-liquid equilibrium existing between Na_3Bi and various alkali halides. Although the studies have only recently been initiated, they have given im-

portant information on the intermetallic species existing in the fused salt solutions.

In a typical experiment a given quantity of pure crystalline Na_3Bi was mixed with the pure alkali halide. The sample was heated to the melting point and then mixed. After this, thermal analysis of the sample was carried out.

For the reciprocal system Na_3Bi and LiCl , a cryoscopic constant of $\frac{4}{3}$ (number of foreign particles per mole) was obtained from the limiting slope of a plot of temperature vs. composition. This indicates that the metathetical reaction

proceeded quantitatively to the right in the lithium chloride solvent. Another feature of these experiments was the evidence that bismuth did not form a polyatomic species in fused salt solutions. A cryoscopic constant of unity (one foreign particle per mole) was obtained for Na_3Bi dissolved in sodium iodide. Zintle et al.³ have presented evidence for complex intermetallic sodium-bismuth species in liquid ammonia.

3. Lithium Hydride-Alkali Halide Solid-Liquid Equilibrium

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

The solid-liquid equilibrium diagram of a binary system gives information about the type and composition of the individual phases which are stable in the system at a given temperature and pressure. Furthermore, these equilibrium data can be used to calculate thermodynamic data describing the binary system. An excellent outline is given by Wagner⁴ of a method for the calculation of thermodynamic functions for each component of a binary system from solid-liquid equilibrium data. We have applied this analysis to the cryoscopic behavior of the lithium halides (Cl^- , Br^- , I^-) and NaCl in

³ Zintle, E., J. Gorbeau, and W. Dullenkopf, Zeitschrift für physikalische Chemie 154A, 1-46 (1931).

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

lithium hydride solutions, the intent being to illustrate the characteristics of the solute in the liquid phase.

The experimental apparatus and procedures have been described in detail in a previous report (ANL-6766, p. 113) in this series. Temperature-composition data for the lithium hydride-lithium chloride (ANL-6766, p. 117; see also Ref. 5), lithium hydride-lithium bromide (ANL-6875, p. 159), and lithium hydride-lithium iodide binary systems have now been obtained over the composition range 0 to 100% lithium hydride. All three systems are simple eutectics. Formation of solid solution was not observed in thermal analysis of the solid-liquid equilibrium mixtures or in X-ray diffraction analysis of the solids. The eutectic compositions and melting points observed are summarized as follows:

<u>System</u>	<u>Eutectic Composition</u> <u>(m/o LiH)</u>	<u>Eutectic Melting</u> <u>Point (°C)</u>
LiH-LiCl	34.0	495.6
LiH-LiBr	29.7	453.3
LiH-LiI	23.5	390.8

In the reciprocal salt system lithium hydride-sodium chloride, the following equilibrium exists, $\text{LiH} + \text{NaCl} \rightleftharpoons \text{LiCl} + \text{NaH}$. The position of this equilibrium is controlled by usual factors, the stable pair being LiH-NaCl. Of particular importance to the execution of the experiments were the stability of sodium hydride, its normal dissociation pressure, and its vapor pressure. Literature data⁶ indicate that NaH has a hydrogen dissociation pressure of about 3000 mm at 600°C. In order to insure the retention of LiH and NaCl in the sample crucible, it was necessary to maintain a hydrogen pressure of about 3000 mm Hg over the sample. Even at these pressures there were some experiments in which appreciable quantities of sodium hydride and sodium metal were found condensed in the cooler portions of the equipment. Generally, however, no more than 50 mg of sodium hydride (1/1000 of the total sample) was distilled in a given experiment. The situation became more critical when the system was rich in sodium chloride. At high concentrations of sodium chloride, the solid-liquid equilibrium temperature increased so that a hydrogen pressure of 3000 mm Hg was no longer sufficient for maintaining the stable pair, LiH and NaCl, in the sample crucible. For operation at these higher temperatures, hydro-

⁵ Johnson, C. E., S. E. Wood and C. E. Crouthamel, J. Inorg. Chem. 3, 1487 (1964).

⁶ Werner, R. C. and T. A. Ciarlariello, Metal Hydride Fuel Cells as Energy Storage Devices, E/Conf. 35/Gen/14, May 23, 1961.

gen pressures which would exceed the safety factor of the apparatus would have to be used. Therefore, the region from 75 to 100 m/o sodium chloride was not examined experimentally.

Thermal analysis studies have now been completed defining the solid-liquid equilibrium temperatures in the lithium hydride-sodium chloride reciprocal system. The lithium hydride-sodium chloride system is a simple eutectic melting at 565.7°C and containing 55.3 m/o lithium hydride. The solid-liquid equilibrium data are plotted in Figure VI-6. No indication

of the formation of a solid solution was obtained from either the thermal analysis data or X-ray powder patterns of the solid phase for this system.

Figure VI-6

LiH-NaCl SOLID-LIQUID
EQUILIBRIUM

In the analysis of these binary diagrams only the heterogeneous equilibrium between pure solid and a binary liquid mixture was considered. With no evidence for solid solution, it was concluded that only pure solid component was precipitating from the mixture. For such a system, the change of the chemical potential on mixing, $\Delta\mu^M$, for the component in solution which was in equilibrium with the pure solid was calculated by the use of the following equation:

$$\Delta\mu_1^M(x_2T_e) = \Delta\tilde{H}_f \left(\frac{T_e - T_m}{T_m} \right) + T_e \int_{T_m}^{T_e} \frac{dT}{T^2} \int_{T_m}^{T_e} \left(\tilde{C}_p^{(l)} - \tilde{C}_p^{(s)} \right) dT$$

In this equation, $\Delta\tilde{H}_f$ is the molar change of enthalpy of the pure component on melting at its melting point, T_m , and T_e is the equilibrium temperature of the two phase system. The standard state of the component in solution was chosen to be the pure supercooled liquid at the equilibrium temperature and one-atmosphere pressure.

It is convenient to express the thermodynamic behavior of the system in terms of the excess chemical potentials defined by the equations

$$\Delta\mu_1^E(x_1) = \Delta\mu_1^M - RT_e \ln(1 - x_2) = RT \ln \gamma_1$$

$$\Delta\mu_2^E(x_2) = \Delta\mu_2^M - RT_e \ln x_2 = RT \ln \gamma_2$$

In examining the cryscopic behavior of each electrolyte dissolving in lithium hydride the following general characteristics were observed. The limiting slope of the experimental data defining the solid-liquid equilibrium approaches a value of $\nu = 1/2$ for the lithium halides in lithium hydride and a value of $\nu = 1$ for the reciprocal system, sodium chloride in lithium hydride, where ν is the total number of particles produced by a molecule of solute.

If it is assumed that the lithium halide is a dimeric species, Li_2X_2 , in very dilute solutions in lithium hydride and that the solution is ideal in terms of the species LiH and Li_2X_2 , the limiting value of the curve of temperature vs composition would be a line with a slope of $\nu = 1/2$. The limiting value of the same function for an ideal solution of LiX (un-ionized) in lithium hydride, or of Li_2X^+ and X^- in lithium hydride would be a line with a slope of $\nu = 1$. The fact that the experimental data approach a line with a slope of $\nu = 1/2$ strongly indicates that the lithium halides exist predominately as the dimeric species in the fused lithium hydride solvent.

A study of the type of species present at higher concentrations of lithium halide in lithium hydride is illustrated in Figure VI-7. The line represents the calculated values of $\Delta\mu_{\text{LiH}}^E$ on the basis of ideal solutions formed by the species Li_2X_2 and LiH . For the three systems, LiH-LiCl , LiH-LiBr , and LiH-LiI , the experimental data follow the calculated line to 0.4 mole fraction. At

Figure VI-7

COMPARISON OF EXPERIMENTAL DATA for $\Delta\mu_{\text{LiH}}^E$ WITH VALUES CALCULATED ASSUMING Li_2X_2 and LiH .

$$\Delta\mu_{\text{LiH}}^E = -RT_e \ln(N_{\text{LiH}} + 1/2N_{\text{LiX}})$$

this point, deviations occur for both the lithium bromide and the lithium iodide systems. It is interesting to note that the experimental values for lithium chloride follow the calculated line even up to a mole fraction of 0.7. Collectively the data give strong indication that the species Li_2X_2 may exist even in somewhat concentrated solutions. However, it must be realized that the solutions are not ideal, and such effects as those due to dispersion forces and volume change are probably present.

The lithium hydride-sodium chloride system shows somewhat different solution properties than the other lithium hydride binaries. Not only are the deviations smaller in magnitude, but they are also dissimilar. $\Delta \mu_{\text{LiH}}^E$ deviates in a positive fashion from ideal solution behavior, while $\Delta \mu_{\text{NaCl}}^E$ deviates in a negative manner. These deviations would indicate that because of the larger Na^+ ion, (as compared to the Li^+ ion) simple ion pair association rather than polymerization is apparently sufficient to stabilize the system.

Assuming that sodium chloride is a monomeric species, NaCl , in very dilute solutions in lithium hydride and that the solution is ideal in terms of the species NaCl and LiH , then the limiting value of the curve of temperature vs composition would be the line marked $\nu = 1$, in Figure VI-6. The limiting value of the same function for an ideal solution of ionized Na^+ and Cl^- ions in lithium hydride would follow a line marked $\nu = 2$. The fact that the data approach the line marked $\nu = 1$ indicates that sodium chloride probably exists as an associated monomeric species in lithium hydride.

The data reported here correlate well with that of Berkowitz and Chupka⁷ who determined the species present in the vapor phase of alkali halide salts when the vapor was in equilibrium with its condensed phase. They report the following dimer-to-monomer ratios: lithium chloride, 2.50; lithium bromide, 2.29; lithium iodide, 1.09; sodium chloride, 0.45. Their data show that polymerization is a general characteristic of lithium salts. However, the predominant species in the vapor phase over sodium, potassium, and rubidium salts are monomers.

4. Regeneration Studies: Sodium-Bismuth

a. Liquid-Vapor Relationships in the Regeneration of the Sodium-Bismuth Cell

A series of sealed-tube experiments provided qualitative information on the relative extent of regeneration which may be achieved by varying the condensation temperature in the regeneration of a sodium-bismuth bimetallic

⁷ Berkowitz, J. and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).

cell. The experiments were conducted by heating Na_3Bi in one end of a sealed tube while maintaining the other end at a lower temperature. The hot-end temperature was maintained at about 900°C ; the cool-end temperature was varied from 525 to 712°C . In each case, the condensate at the cool end was pure sodium. The residues remaining in the hot zone contained from 15 to 62 a/o sodium, corresponding to cool-zone temperatures from 525 to 712°C , respectively. (The original sodium content in the Na_3Bi starting material was 75 a/o.)

From transpiration experiments, the vapor over molten 50-50 a/o Na-Bi alloy at about 900°C was found to contain about 3 to 3.5 a/o bismuth. This concentration of bismuth in the vapor appears to indicate that some fractionation will be necessary in the regeneration cycle of the sodium-bismuth cell. However, the sealed-tube experiments indicate that the simple tube functions as a fractionation column and suffices to provide very pure sodium, i. e., sodium containing less than 40 ppm bismuth.

A significant finding in the sealed-tube experiments was the observation of a band of solid Na_3Bi at an intermediate site in the temperature gradient. This has been interpreted in terms of an isobaric temperature-composition phase diagram. Such a phase diagram for a sufficiently low pressure may contain a region corresponding to equilibrium between vapor and solid Na_3Bi . The practical consequence is that if cell regeneration operates at such a low pressure, solid Na_3Bi may be expected to accumulate and may eventually block the regenerator. The most direct means of avoiding the formation of Na_3Bi is to operate the cell at a sufficiently high pressure. The system pressure may be regarded as being fixed by the temperature at the condensation site in the regenerator together with the composition of the condensate.

Once an isobaric temperature-composition phase diagram representing the system has been established, some conclusions based upon such a diagram become apparent.

- (1) By selecting the composition of material to be returned to the cathode, the hot-zone temperature in the regenerator is fixed.
- (2) By fixing the composition of material withdrawn from the cathode and sent to the regenerator, a unique hot-zone temperature is not established. In this case, if the pressure is to remain at the value for the previously established isobaric phase diagram, a range of possible hot-zone temperatures exists. The lowest value would correspond to the bubble point on the diagram at the selected composition; the highest value would correspond to the dew point. As a practical matter, which is different from the idealized equilibrium situation, operation at a temperature between the bubble and dew points would require

a suitably rapid rate of vapor throughput and condensation to balance the tendency toward increased pressure once the bubble point temperature is exceeded.

- (3) The cell reaction can generally be run at a temperature equal to or below the condensation temperature. It cannot be carried out at a higher temperature unless a pressure gradient exists between the condensation region and the cell.

The above experiments have indicated not only that fractionation may be necessary in the regeneration of the sodium-bismuth cell, but also that the fractionation may be simply achieved. Operation of the regenerator at a sufficiently high operating pressure, and thus a sufficiently high condensation temperature, would be required to avoid the deposition of solid Na_3Bi . Alternatively, some provision might be made for flushing out solid Na_3Bi in the regenerator, perhaps with the fused salt cell electrolyte.

b. Mass Spectrometric Studies of Sodium-Bismuth Vapor

In order to calculate partial vapor pressures expected to exist in the thermal regeneration process of the sodium-bismuth regenerative cell, it is necessary to identify and to obtain vapor pressure data for the various sodium and bismuth species existing in the vapor phase over various alloy compositions which may comprise the cell product. For this purpose, Knudsen effusion experiments using a mass spectrometer for analysis of the vapor are suitable in low temperature ranges where the vapor pressures are low enough. However, at present, some assumptions regarding cross section ratios and fragmentation patterns are necessary in the interpretation of results. Some mass spectrometric experiments have been made. The above qualifying factors, together with the exploratory nature of the work performed so far, serve to limit the reliance to be placed on the numerical values derived from the presently available results. However, some conclusions can be made regarding the feasibility of regeneration of the sodium-bismuth bimetallic cell.

Under the vacuum conditions existing in the mass spectrometer (about 10^{-6} torr), Na_3Bi was found to vaporize by decomposition; no Na-Bi molecular species could be detected in the vapor either in the form of Na_3Bi or NaBi . The sodium ion peak became evident at a temperature of about 273°C . It was only at a temperature of 417°C , some five hours later, that the Bi^+ peak first appeared. In the interval, the atom fraction of sodium in the condensed phase in the cell had dropped from the original value of 0.75 to about 0.6.

In regard to the $\text{Bi}_2 \rightleftharpoons 2 \text{Bi}$ equilibrium which exists in the vapor phase in the Knudsen cell, there are uncertainties in the present interpretation of the mass spectrum which affect somewhat the quantitative value for

total bismuth pressure, but not the qualitative conclusion regarding cell regeneration presented here. Uncertainty in the pressure values stems from assuming (1) that the additivity rule holds for the cross sections (σ) of Bi_2 and Bi for ionization by electron impact and (2) that there is no fragmentation of Bi_2 . The additivity rule is regarded as a good first approximation and states that

$$\frac{\sigma_{\text{Bi}_2}}{\sigma_{\text{Bi}}} = 2.$$

Figure VI-8

PARTIAL PRESSURES OF SODIUM
AND TOTAL BISMUTH vs ATOM
FRACTION SODIUM IN RESIDUAL
CONDENSED PHASE

Partial fragmentation of Bi_2 is likely and would lead to a high apparent value for the Bi^+ ion current. If it is assumed that 60% of Bi_2 is fragmented, the total pressure,

$$P_{\text{Bi}} + P_{\text{Bi}_2},$$

plotted in Figure VI-8, would be raised about 15% in the region where Bi_2 made a significant contribution to the total bismuth pressure, i.e., in the region of the curve falling between about $X_{\text{Na}} = 0.2$ to 0.05 . The part of the curve illustrating the preferential volatilization of sodium would not be affected. This feature provides some

indication that regeneration of a sodium-bismuth cell is feasible.

If the course of the experiment with respect to temperature and composition is traced on the phase diagram, it is found that solid Na_3Bi might be expected to exist only under the conditions existing at the first Bi^+ measurement. At this point (417°C), it may be calculated that for

$$\Delta F^\circ = 69.5 \text{ kcal/mole}$$

or that for

$$\Delta F^\circ = 10.9 \text{ kcal/mole.}$$

If the uncertainty in the partial pressure of monomeric bismuth were as high as one order of magnitude, the uncertainty in the ΔF° values would be ± 3 kcal/mole.

B. Regenerative Emf Cell -- Engineering Studies

Engineering studies are now underway to investigate the feasibility of

developing a practical thermally regenerative emf cell, which would ultimately be suitable for coupling to a reactor or other heat source. Both the bimetallic and lithium hydride cells are being studied.

This work has included experimental studies of "open" sodium-bismuth cells (cells in open-top crucibles) in inert-atmosphere gloveboxes; experimental studies of "closed" sodium-bismuth cells (cells of self-closed construction); experimental studies of corrosion of engineering materials of construction by bismuth, tin, sodium, and molten salts; and engineering thermodynamic studies of sodium-bismuth, sodium-tin, and lithium-tin bimetallic cell systems as well as lithium-hydride cell systems.

1. Sodium-Bismuth "Open" Cell Studies

Experimental sodium-bismuth bimetallic "open" cells (cells in open top crucibles) have been operated with sodium chloride - 62.5 m/o sodium iodide eutectic electrolyte, with and without 5 m/o sodium fluoride; sodium hydroxide electrolyte; and sodium hydroxide - 12 m/o sodium iodide electrolyte. The cells consisted of stainless steel crucibles about 1 7/8-in. dia. by 5 in. high into which the electrolyte was placed. For an experiment, a crucible was placed in a stainless steel well connected to a helium inert-atmosphere box and was heated by a resistance furnace surrounding the well. The cathodes consisted of 7/8-in. ID by 1 1/4-in. deep stainless steel cups with hollow support rods which also served as thermocouple wells and electrical connectors. Bismuth was placed in the cathode cups, which were immersed under the electrolyte. In some experiments, bismuth was placed directly into the 1 7/8-in. dia. crucibles to obtain a larger cathode surface area.

The anodes consisted of stainless steel cups, each with a support rod attached and with a hole in the bottom. Cup holes of 1/4-, 3/8-, and 7/8-in. dia. were used. In most of the experiments, a layer of porous stainless steel sponge was used to cover the holes in the anode cup. In this way the sodium was retained in the cup and yet was allowed to contact the electrolyte when the bottom of the anode cup was dipped slightly into the electrolyte.

The cells have been operated at 575 to 685°C with the sodium chloride-sodium iodide electrolyte and at 300 to 500°C with the sodium hydroxide-sodium iodide electrolyte. With the 7/8-in. dia. anode and 7/8-in. dia. cathode separated by 2 in. of electrolyte, cell resistances of about 3 to 0.15 ohms over the temperature ranges have been experienced. When the electrolyte was allowed to freeze below 575°C, cell resistances of several hundreds of ohms were noted. Currents as great as 560 ma or 145 ma/cm² at 0.28 volt have been drawn from the cells.

a. Open-Circuit Potential of Sodium-Bismuth Cell

In an experiment to determine open circuit voltages, anode and cathode cups consisting of alumina tubes with closed ends were dipped into a sodium chloride-sodium iodide electrolyte contained in a crucible. A small hole about 0.03 in. in dia. was provided in each alumina tube to allow the electrolyte to enter the tubes. Sodium was placed in the anode cup and bismuth-sodium mixtures were placed in the cathode cup. Tantalum rods were used

in the alumina tubes as electrical contacts. Figure VI-9 shows the open-circuit voltages obtained at 586°C as a function of mole fraction of sodium in the bismuth cathode.

Figure VI-9

OPEN-CIRCUIT POTENTIAL OF
SODIUM-BISMUTH CELL AS A
FUNCTION OF m/o Na IN Bi
CATHODE

between the cathode bismuth surface and the anode sodium surface, and a cell electrolyte of sodium chloride-62.5 m/o sodium iodide. In some of the runs 5 m/o sodium fluoride was added to the electrolyte.

b. Non-Faradaic Sodium Transfer

A study was made of the irreversible or non-faradaic transfer, i.e. without corresponding production of cell current, of sodium from anode to cathode. This transfer is the result of the solubility of sodium in the electrolyte. The rate of transfer was measured (1) as a function of temperature at cell open-circuit condition, and (2) as a function of cell current at constant temperature.

The cell had a cathode cup of 7/8-in. ID, an anode with a cup hole of 7/8-in. dia., a distance of 2 in. be-

The non-faradaic transfer is defined as

$$q = \frac{Q - AIt}{t}$$

where q = non-faradaic transfer, g/hr,

Q = total weight (g) of sodium transferred from anode to cathode during run,

$A = (3600)(23)/96,500 = 0.857 \text{ g/(amp)(hr)},$

I = average cell current, amp, and

t = time of run, hr.

Figure VI-10

NON-FARADAIC OR IRREVERSIBLE
SODIUM TRANSFER AND
CONDUCTANCE IN AN OPEN-
CIRCUIT Na-Bi CELL AS A
FUNCTION OF TEMPERATURE

Figure VI-11

NON-FARADAIC OR IRREVERSIBLE
SODIUM TRANSFER IN A Na-Bi
CELL AS A FUNCTION OF CELL
CURRENT AT 585°C

Cell Electrolyte: 63 m/o NaI-37 m/o NaCl

Figures VI-10 and VI-11 show the results of these tests. From these figures, it is noted that the non-faradaic transfer rate increased as the cell temperature was increased and decreased as the cell current was increased. Although the reason is not fully understood for the decrease in non-faradaic transfer rate with increasing cell current, several explanations have been postulated. Among these are the following: (1) the flow of sodium ions from anode to cathode (due to cell current) competes with the flow of sodium atoms from anode to cathode, and (2) there is electronic conduction through the electrolyte. Further study of the non-faradaic transfer as a function of cell current is planned. The addition of 5 m/o sodium fluoride to the electrolyte did not noticeably change this transfer rate. The electrical conductivity (reciprocal of resistance) of the cell is also shown in Figure VI-10 as a function of temperature.

The cell electrical efficiency is a product of the voltage and current efficiencies, which in turn are functions of cell conductance, cell current, and the non-faradaic sodium transfer. Although additional experiments will be required to determine optimum parameters, the work to date indicates that cell current efficiencies of about 80% can be obtained during operation at

75% of the open-circuit voltage. The resulting overall cell electrical efficiency is about 60%.

2. Sodium-Bismuth "Closed" Cell Studies

A closed cell apparatus with 3-in. dia. electrode sections but without a thermally operated regenerator was constructed of stainless steel. This cell has a frozen electrolyte - silicone rubber combination electrical insulator and pressure seal. The silicone rubber pressure seal is placed about 1 1/2 in. beyond the cell between water-cooled flanges which are attached to the cell by 1/32-in. thick discs to minimize heat transfer. An alumina spacer is placed between the 1/32-in. thick discs. The cell body proper is heated by 1/8-in. dia. stainless steel sheathed electrical heating elements.

The cell was charged with 313.6 g of salt electrolyte (31.6 m/o NaCl, 53.2 m/o NaI, and 15.2 m/o NaF) and 400 g of bismuth. The cell was heated to an operating temperature of about 550°C, and a total of 15.5 g of sodium was added to the cell anode. At this time the cell developed a potential of 1.22 volt, a voltage which agrees with the open-circuit cell data from Figure VI-9. A load was placed on the cell, and the cell voltage gradually decreased as the sodium was transferred to the cathode.

In order to continue to operate the cell electrically, it was periodically recharged by reversing the current. The cell was completely discharged a number of times and recharged to voltages as high as 2 1/4 volts. The highest voltage observed on initially adding sodium to the cell was 1.22 volts, which indicates that, on charging the cell to 2 1/4 volts, decomposition of the sodium halide electrolyte may occur and after the recharging operation the recombination may be the driving force for the high voltage.

The cell has been charged and discharged at currents as high as 10 amp. The cell resistance is of the order of 1 to 0.025 ohm depending upon the temperature. At 0.05 ohm, cell resistance voltages of about 0.5 have been obtained at 4 amp discharge current under conditions where the open-circuit potential was about 0.7 volt.

The cell has been at an operating temperature of from 535 to 650°C for over 100 days (as of March 20, 1965). The objectives of continued operation are to determine (1) the effects of operation on the freeze seal-insulator and stainless steel cell and (2) the effects of operating variables, such as temperature and current, on cell behavior. At present the freeze seal-insulator is functioning well and the stainless steel cell shows no evidence of deterioration.

3. Engineering Material Corrosion Studies

In the thermally regenerative bimetallic emf cell systems described in the foregoing sections, the operating temperature of the cell would be about 550°C and that of the regenerator would be well above 800°C. No container materials have yet been found that are readily fabricable, adequately strong mechanically, and sufficiently resistant to corrosion by the proposed bismuth and tin cathode metals at regeneration temperatures.

Although a considerable amount of information is available on alkali metal corrosion from work related to space and fast reactor projects, very little information was found on the corrosion by heavy metals at temperatures above 800°C. It was, therefore, necessary to conduct static tests on various possible container materials selected on the basis of available solubility data. The results of static corrosion tests with bismuth and tin are summarized in Table VI-1. During the tests, the liquid metals were contained in two 70 w/o Mo-30 w/o W crucibles. The crucibles were not visibly attacked by the liquid bismuth or tin. In several of the runs the depths of penetration of the test specimens were determined by electron microprobe analysis.

These static tests indicated that tungsten, 70 w/o Mo-30 w/o W, and possibly tantalum and molybdenum show sufficient promise to warrant dynamic corrosion tests with tin and bismuth. Although the static tests showed that 304 stainless steel resisted corrosion to bismuth, dynamic tests later showed that stainless steel is subject to mass transfer corrosion. The static tests also indicated that further tests of Al_2O_3 as an electrical insulator for bismuth and tin at cell temperatures of about 600°C are warranted.

Following the static tests, dynamic corrosion tests were conducted to determine the effect of liquid bismuth on low carbon steel. Thermal convection loops 10 in. high and 6 in. wide were fabricated from standard 1/4-in. low carbon steel pipe and were thoroughly descaled before the experiments. In a test, liquid bismuth (or sodium-bismuth alloy) was circulated in a loop having a temperature differential of either 100 or 400°C between the hot-leg and cold-leg sections. At the end of an experiment, the loop was dissected radially and the internal cross sectional areas which were exposed to the liquid bismuth were determined by means of enlarged photographs and a planimeter. Minimum thicknesses of the pipe walls were also measured. The results of several loop tests are plotted in Figure VI-12. Other data including temperatures, length of the experiments, and remarks are listed in Table VI-2. The same general pattern of variation in cross sectional areas was observed for all cases in which extensive corrosion occurred

Table VI-1

SUMMARY OF STATIC CORROSION TESTS

Liquid Metal	Test Material	Temperature (°C)	Time (hr)	Remarks
Sn	Ta	900	27	No visible attack
Sn	Ta	1000	96	15- to 20- μ penetration
Sn	Mo	1000	26	10- to 15- μ penetration
Sn	W	1000	96	No visible attack
Sn	Al ₂ O ₃	600	24	Clean and no attack
Sn	Al ₂ O ₃	600	77.5	No visible attack. Sn did not wet specimen
Sn	Al ₂ O ₃	850	29	Slightly wet, no attack
Sn	Al ₂ O ₃	850	76	Completely wet, no visible attack
Sn	Al ₂ O ₃	1000	74	Completely wet, slightly conducting
Bi	304 stainless steel	850	97	No visible attack
Bi	Steel 1020	1000	22	80 μ -thick bismuth intermetallic
Bi	Steel 1020	1000	100	Intergranular penetration
Bi	Al ₂ O ₃	600	99	No visible attack. Bi did not wet specimen
Bi	Al ₂ O ₃	850	52	Partly wet
Bi	Al ₂ O ₃	863	48.5	Slightly wet, no attack
Bi	Al ₂ O ₃	1000	72	Partly wet, no visible attack

Figure VI-12

DYNAMIC CORROSION OF LOW CARBON STEEL IN LIQUID BISMUTH AND BISMUTH-SODIUM ALLOY

Table VI-2

SUMMARY OF DYNAMIC CORROSION TESTS OF LOW CARBON STEEL

Loop No.	Liquid Metal	Temperature (°C)		Time (hr)	Remarks
		Max.	Min.		
2	Bi	520	420	1000	Slightly attacked, less than 0.010 in.
3 ^a	Bi	800	700	24	No visible attack
1	Bi	800	700	100	No visible attack
5	Bi	850	450	279	Leak developed, see Figure VI-12
4	Bi	850	450	430	Leak developed, see Figure VI-12
6	20 a/o Na- 80 a/o Bi	850	450	125	Leak developed, see Figure VI-12

^a The test was terminated after 24 hr because a test coupon which had been inserted in the loop stopped the liquid metal flow.

(see Figure VI-12). A severe dissolution of steel resulting in as much as a 60% increase in the pipe inside cross sectional area was observed at the entrance to the hot-leg region of the loop; this is shown at the 35 to 45 percent axial coordinate in Figure VI-12. A lesser increase appears in the section at the 10 to 25 percent axial coordinate. No significant changes in cross sections appear in the other sections of the loops. Most of the mass-transferred material was found in the form of loose aggregates of metallic crystals. In each run the liquid metal velocity in the loop at the start of the run was about 10 ft/min but after approximately 5 hr of operation it decreased to 1 ft/min. Possible causes of decreased velocity are (1) reduction of cross sectional area due to the formation of precipitates or (2) viscosity changes resulting from the dissolved iron.

These dynamic corrosion tests indicate that low carbon steel is not suitable for use in the high temperature ($\sim 900^{\circ}\text{C}$) regeneration section of a bismuth-sodium system, although it may be suitable for use in the low temperature ($\sim 600^{\circ}\text{C}$) cell operating section.

Corrosion test loops of tantalum, niobium, niobium-1 w/o zirconium, and molybdenum-30 w/o tungsten are being constructed for operation. Loops of tungsten and other refractory metals are also being considered for investigation.

4. Engineering Thermodynamic Studies

Preliminary thermodynamic studies of the regeneration efficiencies for sodium-bismuth, sodium-tin, and lithium-tin bimetallic cell systems and the lithium hydride cell system have been made. During cell operation of the bimetallic systems the anode metal (sodium or lithium) passes as positive ions through the fused salt electrolyte to the cathode, where the anode metal dissolves in the cathode metal (bismuth or tin). In the lithium hydride system lithium is the anode metal; during cell operation it passes as positive ions through the fused salt electrolyte to react with negative hydrogen ions, originating from the hydrogen cathode, to form lithium hydride. Lithium hydride is soluble in the electrolyte and to a lesser extent in the molten lithium anode.

a. Bimetallic Systems

In the bimetallic systems, a portion of the cell cathode metal with some dissolved anode metal is continuously circulated through a regenerator in heat exchange relationship, that is, the hot cathode metal returning from the regenerator to the cell is used to heat the cooler cathode metal going from the cell to the regenerator. In the regenerator, some of the anode metal is separated from the cathode metal by evaporation. The anode metal vapor is condensed and returned to the anode of the cell; the cathode metal, depleted in anode metal, is returned to the cell cathode.

Figure VI-13

TEMPERATURE-ENTROPY DIAGRAM OF THE IDEAL REGENERATION CYCLE FOR BIMETALLIC CELL SYSTEMS

C_{pL} specific heat of anode metal liquid, cal/(mole)(°K)

C_{pV} specific heat of anode metal vapor, cal/(mole)(°K)

$\bar{C}_{pL}$ partial molar specific heat of anode metal in cathode liquid, cal/(mole)(°K)

E cell emf, Volts

F Faraday's constant, 23061 cal/Volt eq

ΔG change in free energy of cell process per mole of anode metal, cal/mole

ΔH change in enthalpy per mole of anode metal, cal/mole

H_{fg} latent heat of condensation of anode metal, cal/mole

n equivalents per mole of anode metal, eq/mole

ΔS change in entropy per mole of anode metal, cal/(mole)(°K)

T temperature, °K

Subscripts

1 refers to anode metal condensing at temperature T_1

2 refers to cell at temperature T_2

3 refers to regeneration at temperature T_3

12, 23, 31 refers to going from 1 to 2, 2 to 3, and 3 to 1

Limited recycle rates of cathode metal to and from the regenerator, heat losses through insulation, non-ideal heat exchange, cell electrical losses, and operation of auxiliary equipment, are some of the factors which combine to reduce the actual cycle thermal efficiency below the ideal cycle efficiency.

The temperature at which the bulk of the heat is rejected (condensing temperature of the anode metal vapor from the regenerator) is determined by the regeneration pressure, which is in turn determined both by the mole fraction of anode metal in the cathode metal being returned from the re-

Figure VI-13 shows a temperature-entropy diagram of the ideal regenerative cycle for bimetallic cell systems in which a volatile anode metal is removed from a much less volatile cathode metal by evaporation. The term "ideal cycle" as used here does not mean the Carnot cycle but means operating the chosen cycle in an ideal manner, i.e., in an adiabatic manner with no heat losses through the heat exchangers, and with a high recycle rate of cathode metal to and from the regenerator. The cell could operate at a temperature equal to, greater than, or less than the anode metal vapor condensing temperature.

In order to limit the recycle rate of the cathode metal to and from the regenerator to a practical value, it is desirable that the concentration limits of alkali metal in the cathode alloy range from about 15 to 40 m/o anode metal and that about 10 m/o anode metal be removed in the regenerator.

The engineering thermodynamic studies indicate that for regeneration in the case of the sodium-bismuth system, reflux would be required in the distillation to obtain sodium sufficiently low in bismuth to be returned to the anode of the cell. It is believed that in the sodium-tin and lithium-tin systems reflux would not be necessary. The requirements of reflux reduce the maximum possible regeneration efficiency below the ideal cycle efficiency.

generator to the cell and by the regeneration temperature. Thus, the condensing temperature increases as the regeneration temperature increases, and the ideal regeneration cycle efficiency is nearly independent of the regeneration temperature for a given mole fraction of anode metal in the cathode. The ideal regeneration cycle efficiency increases as the mole fraction of anode metal in the cathode metal decreases; however, a reasonable cathode metal circulation rate sets a minimum mole fraction of anode metal in the cathode metal. For a given mole fraction of anode metal in the cathode metal, the minimum regeneration temperature, in the case where reflux is not required, is determined by the magnitude of the anode metal partial pressure which is required to obtain reasonable distillation rates. (In the case of liquid metals, a partial pressure of at least 1 mm Hg is usually required for reasonable distillation rates.) In the case where reflux is required in the regenerator, the minimum regeneration temperature may be determined by the necessity to avoid solid phase regions.

Table VI-3 shows computed values of efficiencies for the bimetallic cell systems. The efficiencies are based on a heat utilization efficiency of 75% of that of the ideal cycle for the regenerator and a cell electrical efficiency of 60%. In the case of the sodium-bismuth system an internal reflux ratio of 30% is assumed.

The cell voltage and ideal cycle efficiency increase as the dissolved mole fraction anode metal in the cathode metal is decreased. Hence from considerations of cell voltage and ideal cycle efficiency, low mole fractions of anode metal in the cathode metal are desired, but from considerations of cathode metal circulation rate, regeneration pressure, and regeneration temperature, high values are desired.

b. Lithium Hydride System

In the lithium hydride system the cell product is lithium hydride, which is soluble in the electrolyte and to a lesser extent in the lithium anode metal. The electrolyte (or possibly the lithium anode metal) is circulated to and from the regenerator in heat exchange relationship. In the regenerator, hydride is decomposed into hydrogen and lithium. The hydrogen is returned to the cell cathode and the lithium is returned to the cell anode.

Figure VI-14 shows a temperature-entropy diagram of the ideal regeneration cycle for the lithium hydride cell system where the hydrogen is volatilized from the lithium hydride. The term "ideal cycle" here used is similar to that defined above under bimetallic systems.

In order to limit the recycle rate of the electrolyte to and from the regenerator to a practical value it would be desirable that the electrolyte

TABLE VI-3

COMPUTED EFFICIENCIES FOR BIMETALLIC REGENERATIVE CELL SYSTEMS.

<u>Bimetallic System</u>	<u>Mole Fraction of Anode Metal in Cathode Metal</u>			
	<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.4</u>
<u>Sodium-Bismuth</u>				
Cell open circuit emf, volts, at 586°C	0.74	0.64	0.58	0.53
Efficiency, %				
Regeneration, Ideal Cycle - No Reflux	41	38	36	34
Regeneration, Ideal Cycle - 30% Reflux	29	27	25	23
Regeneration 75% of Ideal Cycle - 30% Reflux	21	20	19	18
System, 60% Cell Electrical Efficiency	13	12	11	10
Estimated Regeneration Temperature (°C) to Avoid Solid Phase Region	1052	1037	1027	1017
<u>Sodium-Tin</u>				
Cell open circuit emf, volts, at 500°C ^a	0.47	0.41	0.36	0.31
Efficiency, %				
Regeneration, Ideal Cycle	30	27	23	20
Regeneration, 75% of Ideal Cycle	22	20	17	15
System, 60% Cell Electrical Efficiency	13	12	10	9
Regeneration Pressure, mm Hg, at 800°C	1.3	5.3	10.0	16.6
Sodium Condensing Temperature, °C, for 800°C Regeneration Temperature	462	512	557	582
<u>Lithium-Tin</u>				
Cell open circuit emf, volts, at 550°C	0.74	0.63	0.58	0.54
Efficiency, %				
Regeneration, Ideal Cycle	27	24	20	17
Regeneration, 75% of Ideal Cycle	20	18	15	13
System, 60% Cell Electrical Efficiency	12	11	9	8
Regeneration Pressure, mm Hg, at 1050°C	0.33	0.75	1.75	3.3
Lithium Condensing Temperature, °C, for 1050°C Regeneration Temperature	687	732	782	817

^a Emf values calculated from free energies given by R. D. Hultgren et al., Thermodynamic Properties of Metals and Alloys, J. Wiley and Sons, 1963, p. 876.

Figure VI-14
TEMPERATURE-ENTROPY
DIAGRAM OF THE IDEAL
REGENERATION CYCLE FOR
HYDRIDE CELL SYSTEMS

C_{pH} specific heat of hydrogen gas, cal/(mole)(°K)

$\bar{C}_{pH} \partial C_{pH} / \partial z$ in the case of regeneration of hydride from the electrolyte, cal/(mole)(°K)

$\bar{C}_{pH} \bar{C}_{pHE} - C_{pL}$ in the case of regeneration of hydride from the lithium anode metals, cal/(mole)(°K)

C_{pL} specific heat of anode metal liquid, cal/(mole)(°K)

C_{pLy} specific heat of anode metal with y mole fraction hydride, cal/(mole)(°K)

$\bar{C}_{pHE}$ partial molar specific heat of hydride in electrolyte liquid (saturated with anode metal), cal/(mole)(°K)

E cell emf, Volts

F Faraday's constant, 23061 cal/Volt eq

ΔG change in free energy of cell process per mole of lithium, cal/mole

ΔH change in enthalpy per mole of lithium or mole of H, cal/mole

n equivalents per mole of lithium or H(-1), eq/cal

ΔS change in entropy per mole of lithium or mole of H, cal/mole

T temperature

y mole fraction hydride in the electrolyte

z mole fraction hydride in the anode metal

Subscripts

2 refers to cell at temperature T_2

3 refers to regeneration at temperature T_3

23, 32 refers to going from 2 to 3 and 3 to 2

The cell efficiency is expected to be lower because of the cell voltage loss due to diffusion of hydrogen through the vanadium diaphragm at the cathode.

The cell voltage increases as the dissolved mole fraction of hydride in the electrolyte is decreased. Hence, from a viewpoint of cell voltage, low mole fractions of hydride in the electrolyte are desired but from the viewpoint of electrolyte recycle to the regenerator high values are desired.

contain about 15 to 25 m/o hydride when going from the cell to the regenerator and that about 10 m/o hydride be decomposed in the regenerator.

In the case of the lithium hydride cell system, the temperature at which the heat is rejected (cell operating temperature) is dependent of the regeneration temperature. However, the hydrogen regeneration pressure increases with increased regeneration temperature and with increased mole fraction of hydride in the electrolyte. The cell emf increases with increased hydrogen pressure; it decreases with increased cell temperature and with increased dissolved mole fraction of hydride in the electrolyte.

The regeneration ideal cycle efficiency is dependent upon the regenerator and cell operating temperatures but is nearly independent of the mole fraction of hydride in the electrolyte. Table VI-4 shows computed values of efficiencies for the lithium hydride system. The efficiencies are based on a heat utilization efficiency of 70% of the ideal cycle for the regenerator and a cell electrical efficiency of 50%. These values of 70% and 50% are less than the corresponding values of 75% and 60% used for the bimetallic systems. The heat utilization efficiency is expected to be lower because of anticipated lower heat transfer coefficients for the electrolyte than for cathode metal.

TABLE VI-4

COMPUTED PERCENT EFFICIENCIES FOR LITHIUM HYDRIDE CELL SYSTEM

Regeneration Temperature (°C)	Cell Temperature (°C)	Cell Open Circuit Emf (volts)		Efficiency (%)		
		10 m/o LiH in Electrolyte	20 m/o LiH in Electrolyte	Ideal Regeneration Cycle	Expected ^a Regeneration	Expected ^b System
927	500	0.25	0.24	35	24	12
	600	0.19	0.18	27	19	9
1027	500	0.29	0.28	41	29	14
	600	0.24	0.23	33	23	11
1127	500	0.33	0.31	45	31	16
	600	0.28	0.26	38	26	13
1227	500	0.36	0.34	48	33	17
	600	0.31	0.30	45	31	15

^a Based on 70% of Ideal Cycle.

^b Expected overall thermal efficiency for the regenerator and cell system based on 70% of ideal cycle and 50% cell electrical efficiency.

The expected overall thermal efficiencies of from 8 to 12% for these thermally regenerative cell systems compare favorably with the expected overall thermal efficiencies of other systems for similar application, for example, mercury vapor cycle, 6 to 10%; thermoelectric cycle, 5%; and thermionic at 1337°C, 8% maximum, and at 1777°C, 16% maximum.

VII. DETERMINATION OF NUCLEAR CONSTANTS

The fast neutron cross section program can be described in terms of the use of cross sections in the calculation of the breeding ratio of a fast reactor. Detailed information is required on the nuclear properties of the fuels, fertile species, and reactor structural materials in order to make more efficient use of the fission reaction.

Specifically, the following data are needed:

- (1) cross sections of structural and control materials for radiative capture,
- (2) cross sections of the primary fissionable and fertile species for capture and for fission, and
- (3) cross sections for reactions which degrade the neutron energy spectrum of the reactor.

A more detailed discussion of the breeding ratio and its relationship to nuclear cross sections can be found in a previous report (ANL-6875, p. 167).

In the present program, several of the above types of reactions have been studied. Work on the measurement of radiative capture cross sections as a function of neutron energy in the range occurring in fast reactors has been continued (see ANL-6875, p. 168). Preparations have also been made for the determination of the ratio of the capture and fission cross sections of uranium and plutonium isotopes in the fast spectrum of EBR-II. Finally, a new program has begun on the determination of neutron inelastic scattering cross sections as a function of neutron energy.

A. Neutron Inelastic Scattering

In the study of nuclear reactors, it is necessary to know the cross sections for reactions which degrade the neutron energy spectrum of the reactor. The main mechanism for this degradation is neutron inelastic scattering ($n, n' \gamma$) in which the neutron after a collision with the target nucleus, leaves the nucleus in an excited state with its own kinetic energy decreased by an amount equal to the energy of the excited state. The excited nucleus then returns to its ground state by emitting one or more gamma rays.

Inelastic scattering cross sections are being studied by measuring the number of gamma rays emitted from the excited states of the target nuclei. The measurements are being made as a function of incident neutron energy and as a function of angle of emission of the gamma rays with respect to the incident neutron direction.

The neutron source is a lithium target bombarded with protons from the 3-MeV Van de Graaff accelerator of the Reactor Physics Division; the gamma-ray detector is a NaI crystal. The most difficult experimental problem in this work is the high background in the NaI crystal. The high background is caused by the interaction of neutrons with the crystal and by the detection of gamma rays other than those from the inelastic scattering reaction. This problem is, to a large part, overcome by using the pulsed proton beam of the Van de Graaff accelerator together with a time-of-flight system which allows the NaI crystal detector to record counts only during that time interval in which the gamma rays from the $(n, n'\gamma)$ reaction are expected to arrive at the detector.

In the present work a study has been made of the gamma rays produced by neutron inelastic scattering in niobium-93, whose energy level diagram is shown in Figure VII-1. Neutron irradiations have been carried out at 13 energies between 0.7 and 1.4 MeV, exciting, in turn, the four niobium-93 levels (0.741, 0.809, 0.958, and 1.080 MeV). For each irradiation, gamma spectra have been obtained and analyzed at an angle of 90° with respect to the proton beam. The cross sections for the production of the 0.741, 0.809, and 0.958 MeV states have been calculated and the results are shown in Figures VII-2, VII-3, and VII-4. Measurements have also been made which will yield the angular distribution of these gamma rays, at two different neutron bombarding energies, but the results are not yet complete.

Figure VII-1

ENERGY LEVELS OF NIOBIUM-93

Figure VII-2

CROSS SECTION FOR PRODUCTION OF 0.741 MeV STATE OF NIOBIUM-93 BY NEUTRON INELASTIC SCATTERING

Figure VII-3

CROSS SECTION FOR PRODUCTION
OF 0.809 MeV STATE OF
NIOBIUM-93 BY NEUTRON
INELASTIC SCATTERING

Figure VII-4

CROSS SECTION FOR PRODUCTION
OF 0.958 MeV STATE OF
NIOBIUM-93 BY NEUTRON
INELASTIC SCATTERING

A major problem in studying gamma rays from nuclear reactions, in addition to the background problem mentioned above, is the analysis of complex gamma-ray spectra. Development work now in progress at ANL is expected to produce a new type of gamma-ray detector, the lithium drifted germanium crystal. This detector, at a sacrifice in counting efficiency as compared with the presently used NaI crystals, will give a large increase in energy resolution. This development will allow gamma rays to be studied to a much higher degree of accuracy by substantially reducing interference from other gamma rays.

B. Radiative Capture

One of the nuclear reactions which absorbs neutrons unproductively in a reactor is radiative capture. The cross sections for radiative capture as a function of neutron energy are needed in order to make proper use of materials proposed for structural and control use in reactors. Further, the study of neutron capture allows one to test theories of nuclear reactions, and to derive information on the spacings and widths of nuclear energy levels. From such information one can then predict other new neutron cross sections in the absence of experimental data.

The neutron energy range of interest in fast reactors lies between about 0.1 keV and several MeV. In the present program, radiative capture has been studied between 4 keV and 3 MeV, covering most of the fast reactor region.

The basic experimental technique used in the capture work is the activation method, wherein the nucleus to be studied is exposed to a monoenergetic neutron beam, and the radioactive species produced thereby are counted with either a beta counter or a gamma-ray analyzer. The counting rate of the activation product is then converted to a capture cross section by suitable calibrations which yield the absolute neutron flux and the absolute disintegration rate of the capture product. The monoenergetic neutron beam is produced by the reaction ${}^7\text{Li} (p,n) {}^7\text{Be}$ and $\text{T} (p,n) {}^3\text{He}$, when lithium and tritium targets are bombarded by protons from the Van de Graaff accelerator. The neutron flux is measured with a fission chamber, which counts fissions in a thin deposit of uranium.

Figure VII-5

In a previous report (ANL-6875, p. 168) neutron capture cross section data were reported for ^{187}Re , ^{158}Gd , and ^{170}Er as a function of neutron energy. More recently the measurements have been extended down to a neutron energy of 4 keV for these three isotopes. In addition, the cross sections of ^{185}Re and the cross sections for the production of the 19-min state of ^{138}Re from ^{187}Re have been measured between 4keV and 3 MeV (see Figure VII-5).

C. Capture to Fission Ratios in EBR-II

In calculations of the long term behavior of reactors it is necessary to know fission and capture cross sections of the uranium and plutonium isotopes which build up through successive captures in the primary fuel isotope. In many cases, presently available experimental techniques do not allow a detailed study of capture and fission cross sections of these species as a function of neutron energy. An alternate approach is to measure the capture-to-fission ratio of an isotope in a typical fast reactor neutron spectrum. Such a program is currently being carried out in EBR-II.

Samples of ^{233}U , ^{235}U , ^{238}U , ^{239}Pu , ^{240}Pu , and ^{242}Pu have been prepared for irradiation in EBR-II, and are now being placed in various positions in the reactor. Following irradiation the samples will be returned to ANL and will be analyzed to determine the number of captures and the number of fissions which have occurred.

VIII. ANALYTICAL CHEMISTRY

The Analytical Chemistry Group provides a broad spectrum of analytical support to the research and development groups of the Chemical Engineering Division. The group includes a large section for elemental analysis, a section for the development of new analytical methods, and sections which specialize in X-ray diffraction and spectroscopy, in gas chromatography, and electron probe microscopy.

During the past year, the elemental analysis section used 111 methods to perform more than 12,000 analyses; the X-ray section determined several hundred diffraction patterns and performed many spectrochemical assays and identifications; the gas chromatography section analyzed the gaseous products from a number of experiments and monitored numerous glovebox atmospheres; the electron probe was used in studies where diffusion, corrosion, and microscopic variation in chemical composition were important.

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

The analytical effort during the year was highlighted by determinations of the fission yields of molybdenum, cerium and ruthenium; the use of both X-ray diffraction and electron probe microscopy for the elucidation of the uranium-zinc phase diagram; an appreciable expansion of the gas chromatographic program; and the integration of electron probe microanalysis into many Divisional programs.

A. Burnup Monitoring in Fast Reactors

The criteria for the selection of a particular fission product to monitor fissions in a nuclear fuel and the choice of technetium-99 as the burnup monitor for EBR-II fuel were discussed in ANL-6875, p. 174. The development of the analytical procedure for technetium-99 and the application of this procedure to the measurement of the uranium-235 fast fission yield of technetium-99 were also discussed.

Determinations of the fast fission yields of other fission products are now being made. Of particular interest are those nuclides which are potentially useful fission monitors for other fast reactor fuels and those nuclides which can be used to determine the source of the fissions in fuels which contain two fissile nuclides.

1. Fission Yields of Molybdenum-95, -97, -98, and -100

The stable molybdenum fission nuclides should be very satisfactory fission monitors for such reactor fuels as uranium carbide and nitride. Spectrophotometric analyses for molybdenum can be readily performed with a precision and accuracy of $\pm 1\%$ when the burnup is as low as 0.1%.

The determination of uranium-235 fast fission yields of molybdenum-95, -97, -98, and -100 is nearly complete. Fuel from the Mark III loading of EBR-I (burnup, $\sim 0.3\%$) has been analyzed spectrophotometrically for its molybdenum content with a precision of $\pm 0.5\%$ (relative); the relative yields of the molybdenum isotopes are currently being determined by mass spectrometric analysis. When this analysis is completed, individual fast fission yields for the four nuclides will be calculated.

2. Fission Yields of Cerium-140 and -142

The stable cerium isotopes, 140 and 142, are also potentially useful fission monitors particularly in oxide fuels where the extreme operating temperature (2000°C) causes the oxides of technetium and molybdenum to diffuse. Both of the cerium nuclides have xenon and cesium precursors but the half lives of these precursors are so short (the longest is cesium-140, $t_{1/2} = 66 \text{ sec}$) that their loss (by diffusion) should be negligible.

The analysis for cerium can be made either spectrophotometrically or mass spectrometrically. The analytical manipulations would, in either case, be handicapped by the activity of cerium-141 (33 day) and/or cerium-144 (285 day), but this problem should not be difficult to overcome.

Cerium has been determined spectrophotometrically in solutions of EBR-I, Mark-III fuel (0.3% burnup) with a precision of $\pm 0.6\%$. Mass spectrometric analysis will provide the relative yields of cerium-140 and cerium-142 as well as the correction for the small amount of cerium-144 still present in the sample.

3. Fission Yields of the Ruthenium and Palladium Nuclides

The stable (or long-lived) fission nuclides of both ruthenium and palladium can be used to ascertain the source of fission in fuels containing both uranium-235 and plutonium-239. The combined yield of ruthenium-101, -102, and -104 is a factor of 1.5 higher for plutonium-239 fission than for uranium-235 fission; the combined yield of palladium-105, -106, -107 and -108 is a factor of 10 higher for plutonium-239 fission. Determinations of the uranium-235 fast fission yields of the ruthenium nuclides are nearly completed; determinations of the palladium yields are planned. Ruthenium is being determined spectrophotometrically using the method described in ANL-6875, p. 175; the isotopic distribution will be determined mass spectrometrically.

B. Chromatographic Analysis

The number and the variety of gas chromatographic analyses requested increased markedly during the past year. Three gas chromatographs are now in operation within the Analytical Group. One instrument is used to analyze samples from inert atmosphere gloveboxes for oxygen, nitrogen, and hydrogen contaminants as low as 1 ppm; the second to detect minor amounts of gaseous reactions products; and the third, a multiple column-multiple detector instrument, to handle the more complex gas mixtures. Outside the Analytical Group another instrument was installed with the assistance of the Analytical Group and it is now in operation.

During the past year two applications of gas chromatography to Divisional research problems, one associated with the study of metal-water reactions and the other with fluorine-bomb calorimetry, have been of particular interest. In the study of metal-water reactions, laser heating of a submilligram amount of aluminum foil in water was used to induce a metal-water reaction. Gas chromatographic analysis of the evolved hydrogen was sufficiently sensitive to detect 0.05 microliter, an amount which correspond to only 0.1% metal-water reaction.

In fluorine bomb calorimetry, gas chromatographic techniques are being developed to assay the gaseous combustion products. In the combustion of such materials as elemental carbon, silicon, sulfur and phosphorus or compounds containing these elements, complete combustion to CF_4 , SiF_4 , SF_6 , and PF_5 respectively does not always occur. By measuring the amount of C_2F_6 , Si_2F_6 , SF_4 or PF_3 formed, appropriate corrections can be applied to the calorimetric data. When hydrogen, carbon, silicon and oxygen are impurities in the material under investigation, the determination of HF , CF_4 , SiF_4 , and CO_2 in the residual atmosphere of the bomb after the combustion enables the calorimetrist to apply corrections for the combustion of these impurities.

C. X-ray Diffraction Studies of the Uranium-Zinc System, $\text{UZn}_{8.5}$ to UZn_{12}

An X-ray powder diffraction study of the uranium-zinc system in the region $\text{UZn}_{8.5}$ - UZn_{12} has shown that in this system there are two distinct yet related structures, one hexagonal and one rhombohedral. In addition, the hexagonal structure is observed to exhibit a range of composition and a stacking disorder.

Diffraction patterns designated rhombohedral can be indexed with lattice parameters $a = 8.981 \text{ \AA}$ and $c = 13.161 \text{ \AA}$. No variation of lattice parameters indicative of a range of composition for this structure has been observed. A range of composition is associated with the hexagonal structure. Lattice constants range from $a = 8.948 \text{ \AA}$ and $c = 8.915 \text{ \AA}$ at the zinc-rich terminus to $a = 8.980 \text{ \AA}$ and $c = 8.785 \text{ \AA}$ at the uranium-rich terminus.

Axial ratios (c/a) range from 0.9963 to 0.9783. An increase in the a -dimension and a decrease in the c -dimension are associated with a decrease in the zinc content of the structure.

Stoichiometries associated with each of these structures are being determined, the details of each of the structures are under investigation, and relationships between these and other analogous structures are being reviewed.

D. X-ray Spectrochemical Analysis of Aluminum Oxide

X-ray spectrochemical procedures have been developed which provide rapid and reliable analyses for a number of elements present in the aluminum oxide beds from the fluoride volatility processes. For uranium-bearing materials, analysis is made directly on finely ground samples; no dissolution or chemical separation is necessary. For plutonium-bearing materials, the finely ground samples are intimately mixed with an equal weight of fine plastic molding powder and cold pressed in a hydraulic press. The resultant smooth, nonfrangible pellet is encased in a Mylar bag before presentation to the X-ray spectrograph. Analysis consists of a comparison of the uranium or plutonium $L\alpha_1$ X-ray emission line intensity with that from a set of similar, chemically analyzed or specially prepared, standards.

Elemental constituents of the various aluminum oxide samples monitored by X-ray spectrochemical procedures and the corresponding detection limits are as follows:

<u>Element</u>	<u>Detection Limit (w/o)</u>
Chromium	0.005
Iron	0.002
Nickel	0.003
Zirconium	0.002
Tin	0.008
Uranium	0.006
Plutonium	0.006

E. Determination of Magnesium in a Number of Alloys

Of the 10,000 or so individual analyses which are performed each year by the general analysis section of the Analytical Group, procedure modifications frequently have to be made before the analysis can be carried out. A typical example of an analysis which was modified a number of times during the past year was the complexometric determination of magnesium with ethylenediaminetetraacetic acid (EDTA). It was necessary to determine from 1 to 70% magnesium in a series of binary alloys. The individual alloying constituents were copper, aluminum, lead, antimony, yttrium, vanadium,

and nickel. Before the titration could be carried out, a means for either complexing or separating the alloying constituent had to be established. Antimony and lead were complexed with mercaptoacetic acid; nickel and copper were complexed with cyanide; aluminum was complexed with triethanolamine; yttrium was separated by an ammoniacal precipitation; and vanadium did not interfere.

F. Electron Probe Microanalysis

An electron probe microanalyzer was placed in operation in the Division during the past year (see Figure VIII-1). With this instrument both

Figure VIII-1

ELECTRON PROBE MICROANALYZER

qualitative and quantitative elemental analyses can be performed in volumes of material as small as one cubic micron. Analysis is accomplished by bombarding the substance of interest with a finely focused beam of electrons (less than 1μ in diameter) and monitoring the wave length and intensity of

the X-rays generated. The method is applicable to all elements having an atomic number higher than that of sodium. Sensitivity is in the range of 10 to 1000 ppm depending upon the element of interest, matrix, and size of the focused electron beam. If adequate standards are available, the relative accuracy is 1 to 2% when the concentration of the element within the volume under consideration is greater than a few percent.

A significant feature of the instrument is the ability to observe elemental distribution in the sample through its scanning presentation. In this mode of operation the electron beam is deflected in both the X and Y directions by electrostatic deflection plates which are synchronized with similar plates of an oscilloscope. Either the characteristic X-ray generated in the sample, the back scattered electrons or the absorbed electrons can be used to modulate the intensity of the oscilloscope trace to give a map of the elemental distribution in the sample. The fraction of the electron beam scattered or absorbed by the sample is a function of the density, topography and mean atomic number of the sample (the higher the atomic number, the higher the back scatter coefficient). Magnifications up to 1800 $\times$ are obtainable by this method.

Corrosion of structural materials is of great interest to the Division, and electron probe microscopy is being used in conjunction with other well established techniques to study this general problem. With the aid of the probe corrosion products can be identified, thickness of corrosion layers can be measured, and corrosion mechanisms can be elucidated. Some of the corrosion problems which have been studied are: the attack of various steels by steam, cadmium-uranium alloys, and bismuth; tantalum by zinc and tin; molybdenum by tin; and niobium and zirconium by steam.

Another use of the probe has been the identification of inclusions in fuels and structural materials. Three samples of high purity uranium dioxide were found to contain, respectively, particles of steel, tantalum, and tungsten ranging in size from 1 to 10 μ . The inclusions were traced to the containers used for the preparation of the fuel material. Examination of the surface of an aluminum alloy fuel plate showed that the intermetallics, AlSi₃, Al₂Si, and Al-Si-Fe, were a significant portion of the grain structure.

The ability of the electron probe to examine microvolumes facilitates the elucidation of phase diagrams, particularly in studies where the diffusion technique is utilized. In a study of the uranium-zinc system, UZn_{8.5} was held in contact with zinc at 672°C for 63 hr. An electron probe micrograph obtained in the course of this study is shown in Figure VIII-2. Four phases were identified: Zn, UZn_{8.5}, UZn_{9.5}, and UZn₁₁. The latter two phases had not previously been observed. It is of interest to note that UZn_{8.5} and UZn_{9.5}, which differ in composition by only 1 w/o are distinguishable using the absorbed electron image.

Figure VIII-2

ELECTRON PROBE ABSORBED ELECTRON IMAGE OF A ZINC-URANIUM ALLOY

A	Zinc
B	UZn _{9.5}
C	UZn ₁₁
D	UZn _{8.5}

The instrument has also been used in a variety of other applications: the determination of the extent of diffusion of fuels into container materials, the examination of fuel pins which had been melted in reactor transients, the identification of minor mineral inclusions in meteorites, and the detection of copper in stainless steel weld failures.

IX. STUDIES AND EVALUATIONS

A. General Objectives

Studies and evaluations are concerned with the feasibility and costs of projected applications of research and development projects of the Chemical Engineering Division. Such studies may show which step of a process should be further modified in order that the process as a whole may be more economical. Or they may show that some particular step or technique has an economic advantage and that new ways of incorporating this step in other process applications should be sought. The scope and specific objectives of these staff studies and evaluations are expected to vary with the interests of the Laboratory.

The present studies and evaluation activities by full-time staff members are a continuance of Division activities previously carried on by ad hoc committees. The major activities during this year have been concerned with two projects: (1) a Divisional economic study of fuels and reprocessing methods for fast reactors and (2) a contribution to an interdivisional conceptual design study and a feasibility and economic analysis of a large metal-fuel fast breeder power reactor and its integrated fuel cycle system.

Future projects are to be defined for studies and evaluations in the area of fuel cycle operations (especially for fast reactors) and allied process applications.

B. Cost Evaluation of Metal-Fueled Fast Reactors

An interdivisional study group has been organized to evaluate the economy of the generation of electric power by a large metal-fueled fast breeder reactor. A report is being prepared for the use of the U.S. Atomic Energy Commission in which the estimated costs of nuclear power generation by metal-fueled reactors are compared with those reported previously for fast breeder reactors fueled with oxide and carbide fuels.¹⁻⁴

-
- ¹ Allis-Chalmers, Atomic Power Development Associates, Babcock and Wilcox Company, Large Fast Reactor Design Study, ACNP-64503, January 1964.
 - ² Combustion Engineering, Liquid Metal Fast Breeder Reactor Design Study, CEND-200, January 1964.
 - ³ General Electric Company, Liquid Metal Fast Breeder Reactor Design Study, GEAP-4418, January 1964.
 - ⁴ Westinghouse, Liquid Metal Fast Breeder Reactor Design Study, WCAP-3251-1, January 1964.

The report will encompass all on-site costs for a 1000 Mw(e) plant including the reactor, integral pyrochemical processing, refabrication, interim on-site storage of wastes, and in addition, the ultimate disposal of high activity level wastes at a separate site. Design criteria and specifications have been established for the ANL Reference Metal Fueled Reactor and Integral Fuel Cycle Facility. The ANL Chemical Engineering Division and the Metallurgy Division were assigned the responsibility for the conceptual design and estimation of the cost of the Integral Fuel Cycle Facility. The key specifications of the reference reactor which establish the fuel reprocessing requirements are presented in Table IX-1.

Table IX-1

SPECIFICATIONS OF THE ARGONNE REFERENCE METAL-FUELED FAST
BREEDER REACTOR WHICH ESTABLISH THE FUEL PROCESSING
REQUIREMENTS.

Total Thermal Power, Mw(t)	2513
Net Electrical Power, Mw(e)	1000
Fraction of Total Power Generated in Core	0.87
Total Breeding Ratio	1.55
Internal Breeding Ratio	0.63
Initial Composition of Fuel, w/o:	
<u>Core</u>	
Uranium	79.30
Plutonium	18.75
Titanium	1.95
<u>Blanket</u>	
Depleted Uranium	100
Core Fuel Burnup, percent of actinides	5.5
Blanket Fuel Burnup, percent of actinides	0.32
Composition of Discharged Fuel, w/o:	0.32
<u>Core</u>	
Uranium	75.11
Plutonium	17.55
Titanium	1.95
Fission Products	5.39
<u>Blanket</u>	
Uranium	97.72
Plutonium	1.96
Fission Products	0.32
Reactor Cycle, days	191
Plant Factor, %	80
Quantity of Fuel Discharged per Cycle, kg	
Core	6252
Blanket	15570

1. Reference Compact Pyrochemical Process for Metal Fast Reactor Fuel

A conceptual process for the decontamination of fuel discharged from a metal-fueled fast breeder reactor and the recovery of plutonium bred in the blanket fuel for use in the refabrication of core fuel elements is described by the flowsheet in Figure IX-1. This flowsheet is for the processing of fuel from a reactor that employs uranium-plutonium alloy in the core

Figure IX-1

PRINCIPAL STEPS IN THE REFERENCE COMPACT PYROCHEMICAL PROCESS FOR METAL FUEL (U-Pu Core; U Blanket)

* TITANIUM, IF A COMPONENT OF THE CORE ALLOY, IS ELIMINATED WITH THE FPN II.
 ** THE RESIDUAL AMOUNT OF FISSION PRODUCT ELEMENTS IN THE PRODUCTS IS BASED ON 0.324 WT. PERCENT FISSION PRODUCTS IN DISCHARGED BLANKET FUEL.

and uranium in the blanket. It is also applicable to alloys containing titanium and/or zirconium as a major component of the core fuel. The flowsheet does not represent the only process steps that would satisfy the processing requirements. Alternative process steps are currently being studied and it is expected that some of these will ultimately lead to more economical processing. However, the reference flowsheet was chosen because it consists of an assemblage of pyrochemical steps for which sufficient supporting evidence

is available from laboratory and pilot plant studies to provide a high degree of confidence in the technical feasibility of the steps, and for which enough information is available from component development studies to develop conceptual equipment designs for use in the estimation of processing costs.

2. Preparation of Fuel for Processing

Preliminary operations are employed to prepare the fuel for processing. The core and blanket fuel assemblies are removed from the reactor and transferred to a sodium-cooled tank where they are retained for about 15 days. During the total period of cooling before reprocessing (20 or more days), the heat generation rate from the decay of fission products decreases by a factor of about 10, and affords a substantial reduction in the heat removal requirements in subsequent process steps. Unlike aqueous processing, the influent streams in pyrochemical processing are not subject to radiation damage, and therefore an extended period of cooling is not required. After cooling, the fuel assemblies are steam cleaned to remove residual sodium and then disassembled and the excess structural metal removed and discarded.

3. Removal of Fission Products

Removal of Fission Products from Core Fuel. In the flowsheet and in the tabulated data, the principal fission products are grouped as follows:

Fission products, volatile (FPV)	Xe, Kr, Te, I
Fission products, salt-soluble, group I, (FPSI)	Rb, Cs, Sr, Ba
Fission products, salt-soluble, group II (FPSII)	Rare earths and Y
Fission products, noble metals, group I (FPNI)	Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb
Fission products, noble metals, group II (FPNII)	Zr, Nb

The core and blanket fuel are processed separately in the initial process steps. The core fuel is treated to remove all fission products listed above. The reference flowsheet is expected to provide greater than 99% removal of the fission products. Because of the presence of residual amounts of fission products in the fuel processed by this reference process, remote refabrication of core and blanket fuel elements and remote refueling of the reactor is necessary.

Declad core fuel is melted in a beryllia crucible and contacted with a fused salt containing magnesium chloride at 1250°C. Of the separate classes of fission products cited above, the FPV products are volatilized, and the FPSI and FPSII groups are oxidized by the magnesium chloride and extracted into the salt phase. The salt phase is separated and the partially processed metal is further treated to remove the FPNI and FPNII fission products in subsequent processing steps.

The FPNI group of fission products is separated from uranium, plutonium, and the FPNII fission products by treatment of the mixture with cadmium chloride in a tungsten crucible at 650°C. Uranium, plutonium, and the FPNII group are chlorinated. The FPNI group is not chlorinated and is accumulated in the cadmium metal phase which is formed as a consequence of the reduction of cadmium chloride.

The immiscible metal and salt phases are allowed to separate by the difference in their densities. The metal phase containing the FPNI fission products is transferred to a waste receiver, and the salt phase containing the uranium and plutonium and FPNII fission products is transferred to the vessel used for blanket dissolution. Further process steps for the combined core and blanket fuel are described below.

Removal of Fission Products from Blanket Fuel and Reduction of Core Fuel. Declad blanket fuel is dissolved in a liquid metal mixture of cadmium, zinc, and magnesium. Simultaneously, uranium and plutonium in solution in the salt phase from the core fuel chlorination are reduced by the magnesium in the solvent metal. This process step is conducted at 650°C in a 405 stainless steel crucible. Fission products of groups FPV and FPNII (the latter from both the core and blanket) are separated by volatilization. The FPSI fission products are separated by extraction into the salt phase. The salt composition is critical for the volatilization step. From presently available data, the composition 60 m/o $MgCl_2$ -25 m/o $NaCl$ -15 m/o KCl is believed to be satisfactory. The other fission products in the blanket, namely the FPSII and FPNI groups, are not separated and accompany the uranium and plutonium in the solvent metal phase. Titanium, if it is a component in core fuel alloy, is volatilized with the FPNII group.

4. Partitioning of Uranium and Plutonium; Recovery of Uranium and Plutonium as Ingots of Metal

Uranium and plutonium are partitioned in a retorting step. The solvent metal phase from the blanket dissolution step, which contains the uranium and plutonium recovered from the core and blanket fuel, is retorted in a beryllia crucible to volatilize cadmium and zinc. Uranium precipitates because of its negligible solubility in the magnesium solution that remains. The FPNI group of fission products from the blanket fuel accompanies the uranium. Plutonium and the FPSII group remain in solution in the magnesium phase which is processed in a separate retort furnace for the ultimate recovery of metallic plutonium. The solvent metals volatilized in the retort operations are recycled to the blanket dissolution step.

The precipitated uranium is retorted in a vessel for uranium retorting to an ultimate temperature of 1200°C to remove the residual solvent metal and to consolidate the uranium into an ingot of metal. The plutonium solution is similarly treated in its retort furnace.

5. Composition of Recovered Uranium Ingots and Plutonium Ingots

The products of the reference flowsheet contain the fission products FPSII and FPNI that were generated in the blanket. The blanket burnup specification for the Argonne Reference Reactor is:

<u>Zone</u>	<u>Blanket Burnup (% of U Atoms)</u>	<u>Quantity of Fuel Removed per Cycle (kg)</u>
Axial Blanket	0.27	5730
Inner Radial Blanket	0.27	1420
Outer Radial Blanket	0.37	8420

For the above conditions the composition of the separate products of the processing is estimated to be:

<u>Uranium Product</u>		<u>Plutonium Product</u>	
<u>Uranium (w/o)</u>	<u>FPNI Fission Products (w/o)</u>	<u>Plutonium (w/o)</u>	<u>FPSII Fission Products (w/o)</u>
99.9	0.1	99.1	0.9

On repeated recycle, the FPNI content of the uranium product will build up slowly and may be expected to reach 0.72% after eight radial blanket cycles (34 yr of irradiation). The FPSII concentration in the plutonium product will not build up because the fission products are removed in the processing of core fuel.

6. Estimated Fuel Cycle Costs for the Argonne Reference Metal-Fueled Reactor

Estimates of operating costs, annual charges, and unit fuel cycle costs have been developed for the integral fuel cycle facility associated with the Argonne Reference Reactor. The costs of processing and waste disposal were estimated by the Chemical Engineering Division and those for refabrication by the Metallurgy Division. The conceptual design of a plant to process fuel as specified in the reference flowsheet was based on the EBR-II Fuel Cycle Facility. All processing and refabrication operations with highly irradiated fuel are conducted remotely in a large heavily shielded inert atmosphere enclosure. Building and installation cost estimates were largely based on the costs incurred in the construction of the EBR-II Fuel Cycle Facility. Equipment cost estimates were based on the cost of equipment for the EBR-II, the projected cost of plant-scale versions of components currently under development by the Chemical Engineering Division, and manufacturers' quotes.

The estimated unit fuel cycle cost for the Argonne Reference Metal-Fueled Reactor is 0.95 mill/kw(e)-hr. A breakdown of this cost is presented in Table IX-2. The unit cost includes amounts for the return on investment,

Table IX-2

COSTS OF THE REFERENCE COMPACT PYROCHEMICAL FUEL CYCLE
FACILITY FOR THE ARGONNE REFERENCE METAL-FUELED
1000 Mw(e) FAST REACTOR

	Unit Costs	
	mills/kw(e)-hr	\$/kg
Processing and Refabrication	1.02	170
Waste Disposal	0.05	8
Out-of-Reactor Fuel Inventory	0.22	38
One Percent Processing Loss	0.03	5
Plutonium Credit	-0.37	-62
Total	0.95	159

the replacement of capital and the operating costs. A breakdown of the annual charges is presented in Table IX-3. A 6.75 percent cost of money

Table IX-3

ANNUAL CHARGES FOR THE REFERENCE COMPACT PYROCHEMICAL
FUEL CYCLE FACILITY FOR THE ARGONNE REFERENCE
METAL-FUELED 1000 Mw(e) FAST REACTOR

Operating Cost	\$4,712,500
Cost of Capital Replacement	654,400
Return on Investment ^a	2,190,900
Inventory Charges	1,577,000
Total Annual Charge	\$9,134,800

^a The total investment includes plant facilities, contractor's overhead and engineering fees, insurance, site improvement, direct installation costs, start-up costs, and working capital.

was used in computing the capital replacement cost. For the return on investment a rate of 13 percent was used which includes taxes, insurance and the cost of money. These percentage values were based on practices of private utility companies, as reported in the AEC Guide to Nuclear Power Cost Evaluation (TID-7025). The depreciation schedules for the replace-

ment of capital was 30 yr for buildings, 15 yr for out-of-cell and in-cell nonprocess equipment, and 5 yr for process equipment.

The reference fuel cycle facility is operated at a plant factor of only 37 percent, principally because reactor unloading, cooling, processing, refabrication, and refueling must occur in the 191-day period between reactor cycles. Consequently, the processing campaign is of 147-day duration per cycle. By increasing the processing plant factor to 80 percent, the output of three reactors totaling 2500 Mw(e) could be handled in the reference fuel cycle facility with only a modest increase in the annual charge, but with a substantial decrease in the unit charge for processing and refabrication. The unit charges for this case appear in Table IX-4. Since the out-of-reactor inventory of the fuel cycle does not increase when a favorable schedule is used with three reactors, the unit inventory charge also is decreased.

Table IX-4

UNIT COSTS OF THE REFERENCE COMPACT PYROCHEMICAL FUEL
CYCLE FACILITY FOR THREE METAL-FUELED FAST BREEDER
REACTORS (2500 Mw(e) TOTAL)

	Unit Costs	
	mills/kw(e)-hr	\$/kg
Processing and Refabrication	0.83	138
Waste Disposal	0.05	8
Out-of-Reactor Fuel Inventory	0.10	17
One Percent Processing Loss	0.03	5
Plutonium Credit	-0.37	-62
Total	0.63	106

C. Divisional Study of Reprocessing of Fast Reactor Plutonium Fuels

The purpose of this study is to compare the cost of processing various fast reactor plutonium fuels by alternative processing methods under a consistent set of requirements and restrictions. The set of conditions includes parameters for reactor power, burnup, and other parameters that are expected to correspond to the range of possibilities as to fuel loads, technical specifications, and economic requirements of a projected fast breeder reactor system capable of producing competitively priced electrical power in 1980. The alternative fuels and processes are those whose technical details are being defined and whose practical applications are being demonstrated in current development programs. Three fuel materials are being considered: metal, oxide, and carbide. For each of the reference fuels, three alternative methods are being considered for the recovery of valuable

fuel from fission products. The three methods are: (1) an aqueous-solvent extraction, (2) a fluid-bed volatility process, and (3) a compact pyrochemical process. All of the above combinations are being examined for two processing plant sizes, corresponding to different sizes of fast reactor power systems, namely, a single 1000 Mw(e) reactor and ten 1000 Mw(e) reactors. For each of the above reactor systems, the process plant loads also vary in uranium and plutonium throughput according to several reactor design and operation conditions, i. e., various cases of fuel burnup, of plutonium concentration in the discharged core material, and of plutonium concentration in the discharged blanket materials.

Although this study is undergoing revision and the cost evaluations should therefore be considered preliminary, current results are summarized here for the purpose of identifying the variables involved in the comparison of alternative fuels and processes and showing the approximate relative contribution of reprocessing, shipping, and out-of-reactor fuel inventory to the total fuel cycle costs.

1. Comparative Cost Analysis

Reference flowsheets for aqueous-solvent extraction, fluid-bed volatility, and pyrochemical processes were selected to serve as a basis for plant cost calculations. Process flow rates, plant size, costs of supplies, services, and chemicals, waste volumes and costs, nuclear safety procedures and other process decisions were based on these flowsheets. The reference reprocessing plants were based on total throughputs of 100 to 1000 kg per day. This range of production covers the total throughput for both the integral processing plant (for one reactor) and the central processing plant (for ten reactors).

The aqueous solvent extraction process is the most highly developed of the three reference processes and could be applied to the specific fuels and processing rates discussed with little change in the flowsheets adopted. However, there are several points in the aqueous process in which this application goes beyond present plant practice:

1. Plutonium enrichment is higher for these fast reactor fuels than for the feed in present aqueous plants, and more difficult criticality problems exist.
2. Solvent degradation under high radiation fields for high burnup fuels is a problem believed to be overcome in the aqueous flow-sheet used here by specifying a 120-day fuel cooling period before processing. (Although this cooling time is longer than that specified in this study for the nonaqueous processes, the higher associated cost is at least partially compensated for by other plant savings, for example, less expensive iodine-handling

steps for longer-cooled fuel and a lower cost solvent treatment for recycle.)

3. Some complications may be offered to the metal-dissolution step by the presence of alloying agents such as ruthenium, molybdenum, zirconium, and titanium.
4. The presently existing processes for conversion of plutonium oxide to carbide is not yet well developed, although promising developments are underway at Argonne National Laboratory and elsewhere.

The fluid-bed fluoride volatility process is less well developed than the aqueous process, and modifications of the reference flowsheet can be expected in reducing this process to practice. Although the major process steps have been given considerable study at several sites in connection with processing of uranium fuel, plutonium behavior is still less well defined than uranium behavior.

The compact pyrochemical process flowsheets are not as highly developed as the aqueous flowsheet, but all the major steps are under study at Argonne National Laboratory. The metal fuel flowsheet is being reduced to practice at the EBR-II integrated processing facility at the Idaho site. The basic plant concepts for pyrochemical processing, including the associated remote operation and maintenance techniques, are being evaluated at the EBR-II plant.

For each of the three processes, capital and operating costs were calculated for direct processing, shipping, inventory, waste disposal, and process losses. The overall cost associated with reprocessing was taken as the sum of costs in these categories.

The following preliminary conclusions appear from the cost analysis of the cases outlined above. The distinction is made here between direct costs of reprocessing and overall costs of reprocessing and associated handling, which includes losses, inventory charges, shipping costs, and waste disposal, as well as the direct reprocessing costs.

1. Large 10,000 Mw(e) central plants have lower overall and direct unit costs (mills/kw-hr) than do small 1000 Mw(e) integrated plants for all cases calculated. Here it is assumed that shipping by presently acceptable methods will continue to be possible. On this basis, the lower direct processing costs for large plants more than compensate for the cost of shipping.
2. For metal fuels, pyrochemical processes have the lowest direct and overall reprocessing costs, regardless of plant throughout

and other variables. This is due to the relative simplicity of the compact pyrochemical process, and the fact that it yields a metal product directly.

3. Waste disposal costs for all cases were lowest for the volatility process, chiefly due to its production of a very low volume solid waste. In some cases, waste disposal for the pyrochemical process was equally low.
4. Fuel inventory and waste disposal for the aqueous solvent extraction process showed substantially the highest costs in all cases. These high costs are due to the relatively long cooling time for the fuel before processing and to the relatively large volumes of process liquid waste, which must be concentrated and solidified.
5. Cost comparisons* of the aqueous, volatility, and pyrochemical processes are as follows:

A. Metal Fuel

1. Small Integral Plant

	<u>High Cost</u>		<u>Low Cost</u>
a. Direct Processing:	aqueous	volatility	pyrochem.
b. Overall Processing and Handling:	aqueous	volatility	pyrochem.

2. Large Central Plant

a. Direct Processing:	aqueous		pyrochem.
	volatility		
b. Overall Processing and Handling:	aqueous	volatility	pyrochem.

B. Oxide Fuel

1. Small Integral Plant

a. Direct Processing:	pyrochem.		volatility
	aqueous		
b. Overall Processing and Handling:	aqueous	pyrochem.	volatility

* Only horizontal comparisons are valid.

2. Large Central Plant

a. Direct Processing:

volatility
aqueous
pyrochem.

b. Overall Processing
and Handling:

aqueous

volatility
pyrochem.

C. Carbide Fuel1. Small Plant

a. Direct Processing:

aqueous

volatility pyrochem.

b. Overall Processing
and Handling:

aqueous

pyrochem. volatility

2. Large Plant

a. Direct Processing:

volatility
aqueous

pyrochem.

b. Overall Processing
and Handling:

aqueous

volatility
pyrochem.

2. The Cost-Throughput Relation for Reprocessing Plants: The Effect of Burnup

If the form of the relation between mass throughput (w) and total annual cost (C) is assumed to be of exponential relation $C = a w^b$, where a and b are constants, then the constant b is found to be approximately 0.5 for the total annual direct processing costs developed for the reference 100 and 1000 kg/day reprocessing plants.

Since the reprocessing plant throughput is furnished by the rate of discharge of fuel, the core fuel processing rate for a reactor of given power is inversely proportional to burnup. Similarly, the blanket processing rate is inversely proportional to the amount (and therefore the concentration) of plutonium bred in the blanket at the time of discharge.

The unit processing costs, mills/kw(e)-hr, for the reference plants were calculated for various burnups and blanket plutonium concentrations by using the above processing cost-load factor b and the appropriate processing rates. As long as combined fuel and blanket processing is assumed, such variations of throughput do not change the relative cost advantages (cited above) for the reference processing plants of 100 and 1000 kg/day capacity. However, the fraction of the total unit fuel cycle cost that is due to the direct processing cost in general varies with this change of throughput because of change of burnup.

The general relation of fuel burnup to processing loads and costs may be described in the following terms. The processing load (w) is directly

proportional to the rate of power generation (P) and inversely proportional to the percent burnup (B), other things being equal. Thus, for two reactors,

$$\frac{w_2}{w_1} = \frac{P_2}{P_1} \frac{B_1}{B_2} .$$

From our previous relation between cost (C) and throughput (w):

$$\frac{C_2}{C_1} = \left(\frac{w_2}{w_1} \right)^{0.5} .$$

Thus, for a given total power generation,

$$P_1 = P_2 , \text{ and } \frac{C_2}{C_1} = \left(\frac{B_1}{B_2} \right)^{0.5} .$$

The significance of this relation is that for a given level of total power generation, the unit costs of reprocessing (in mills/kw(e)-hr) varies not inversely to the first power of burnup, but inversely to the 0.5 power, or whatever power is correct for the cost-throughput relation of the reprocessing plant. Actually, the effect of core fuel burnup on processing costs is even less pronounced because the blanket portion of the processing rate is not changed in general by variations in core fuel burnup.

3. Shipping and Inventory Costs

A study of shipping and out-of-reactor fuel inventory costs was made for aqueous, volatility, and pyrochemical processing of fast reactor fuel. The study compared costs for an integrated processing plant for a single 1000 Mw(e) reactor and a central plant large enough to process the fuel of 10 such reactors. Burnup of core fuel and plutonium concentrations were examined as additional parameters. The assumption was made that presently acceptable rail shipments are feasible for spent reactor fuel.

Shipping and inventory costs were analyzed together because of the interrelationship between the two costs. The value of the fuel affects both the property insurance cost during shipping and the inventory cost. The shipping costs affect the value of the fuel prior to shipping and, thus, the inventory cost prior to shipping. Finally, for pyrochemical and volatility processing, the combined cost of shipping plus inventory has a minimum value for an optimum cooling period which varies with burnup, plutonium concentration in the discharged fuel, and the cost of plutonium. (However, in this study only a single set of fuel values was used: \$10/g fissile plutonium and \$10/kg other actinides.) Other variables have only a minor effect on this optimum cooling time.

Shipping costs for high-burnup, short-cooled fast reactor fuels cannot be taken directly from cost correlations developed for thermal reactors in terms of cost per kilogram of material shipped because of the higher rate of heat dissipation of fission products in the fast reactor fuel. That is, the cask cooling requirement for the present case of fast reactor fuel is more restrictive as to the cask capacity than is the volume or weight of fuel. The shipping cost, therefore, is more directly a function of the amount of heat which must be dissipated than of the weight of fuel shipped.

In this study of fuel shipping costs for spent fuel of fast reactors the cost estimates were made for rail shipments of casks for delivering spent fuel to the reprocessing plant and separate shipments for delivering new fuel to the reactor. It was found more economical to ship empty casks on the return trip than to hold casks at the reactors.

The conceptual cask design for fast reactor fuels employed a heavy internal basket for neutronic isolation and heat conduction. Natural air conduction is used internally and forced air convection externally. However, natural air convection externally is satisfactory in an emergency. In general, cask loading was determined by the actual heating value of the fuel. An external crash buffer (25 tons) is employed for additional safety.

A daily use charge was determined for the spent fuel casks on the basis shown in Table IX-5. A similar basis was used to determine a daily charge of \$140 for the cask for shipping refabricated fuel; this latter cask was lighter, 70 tons total, with a 3000 kg capacity. Estimated costs for round trip shipments for both types of fuel are shown in Table IX-5.

Liability insurance during shipment was estimated at \$1000 per trip plus \$1 per mile for spent fuel and \$500 per trip plus \$0.50 per mile for refabricated fuel.

Property insurance during shipping was estimated at 0.15% of the basic fuel value for the 500-mile distance and 0.20% of the basic fuel value for the 1000-mile distance. The basic fuel values taken in this study were \$10/g for fissile plutonium and \$10/kg for fertile actinides.

Fuel inventory costs were based on annual fixed charges on fuel value of 13%, following the practice of private utilities for nondepreciating capital cited in the AEC "Guide to Nuclear Power Cost Evaluation" (TID-7025).

Since the basic fuel value was taken to apply to fuel material ready for fabrication, adjustments in value were required for fuel in other stages of the fuel cycle operations. These adjustments depend on costs incurred in reprocessing, shipping, insurance, and refabrication, together with costs due to losses. Only approximate adjustments were made in this study.

Table IX-5

FUEL SHIPPING CASK FOR SPENT FAST REACTOR FUEL

<u>A. Cask Characteristics</u>	
Weight, loaded, tons	100
Weight of cask shock buffer, tons	25
Capacity	
Full loading, actinides plus fission products, kg	2000
Heat dissipation, kw	50
 <u>B. Interest, Depreciation, and Insurance</u>	
	<u>% of Cask Cost</u>
Return on investment	6.75
Sinking fund factor (10 years at 6.75%)	7.33
Income tax	3.40
State and local taxes	2.45
Property insurance on cask	1.00
	<u>20.93</u>
 <u>C. Use Charge</u>	
Annual cost of cask and buffer ^a	\$52,000
Annual cost of repairs and supplies	<u>3,000</u>
 Total annual cost	 \$55,000
Use Charge (60% use factor)	\$250/day

^a Total cost of cask and buffer is \$250,000.

The inventory costs for integral (on-site) plants were based on a cooling period of 200 days for aqueous processing with a period after cooling of 160 days. The total time of 360 days corresponds to two reactor unloading cycles in this study. For volatility and pyrochemical processing in integral plants the cooling time was 60 days and the post-cooling period 120 days (one reactor unloading cycle).

The inventory costs for central plants were based on a cooling period of at least 120 days prior to processing for aqueous plants, and it was assumed that longer cooling had no advantage in processing costs. For volatility and pyrochemical processes it was considered that a minimum cooling time of 20 days was required for handling and that longer times had no influence on the cost of processing. However, cooling times somewhat longer than 20 days were used for the central plant using volatility and pyrochemical processing, since the cooling times were selected as optimized values, giving the lowest total inventory and shipping costs. This

calculation involved finding the minima of functions relating cooling time to the heat emission and to the inventory and shipping costs of the fuel.

The costs of inventory and shipping for various fuel recovery processes are summarized in Table IX-6. For aqueous processing there

Table IX-6

COSTS OF INVENTORY AND SHIPPING FOR VARIOUS
FUEL RECOVERY PROCESSES

One-thousand Mw(e) reactor, 80% load factor, 20% total plutonium in core fuel, 2% total plutonium in blanket fuel, fissile plutonium valued at \$10/g, fertile actinides valued at \$10/kg.

Burnup(%)	Aqueous Processing(mills/kw-hr)			Pyrochemical and Volatility Processing (mills/kw-hr)		
	On-Site Plant ^a	Central Plant at Distance Given		On-Site Plant ^a	Central Plant at Distance Given	
		500 miles	1000 miles		500 miles	1000 miles
3	0.547	0.374	0.417	0.280	0.311	0.378
5	0.339	0.246	0.276	0.176	0.213	0.255
10	0.184	0.144	0.164	0.098	0.126	0.151
20	0.106	0.091	0.104	0.059	0.079	0.093

^a No shipping required.

is no incentive for on-site processing (integral plants) because the long out-of-reactor period for the integral plant results in inventory costs higher than the combined inventory and shipping cost for central plant processing. For pyrochemical and volatility processing, the combined inventory and shipping charges for central plants are substantially higher than for integral plants, even of the small 1000 Mw(e) size of this study. However, in determining the overall comparative costs of integral and central plants, the lower unit costs of reprocessing and waste disposal for central plants must be taken into account.

4. Fuel Inventory Costs: Effect of Burnup and Out-of-Reactor Residence Time

The relation of fuel inventory costs to burnup and time required for a complete fuel cycle operation may be illustrated by the following considerations. The power density, H , of the reactor per kg of actinide fuel, L , may be expressed as follows:

$$H = \frac{0.95B}{T} = \frac{Pf}{L} \quad ,$$

where H = reactor power density, Mw(t)/kg fuel in reactor
 0.95 = conversion factor, Mw(t)/kg of fuel fissioned per day
 B = burnup of fuel, weight fraction
 T = irradiation time of fuel in reactor, days
 P = nominal reactor power, Mw(t)
 f = power factor, fraction of total time that reactor is on power
 L = fuel loading in reactor, kg

The rate of fuel discharged from the reactor in kg/day is w , and

$$w = \frac{L}{T} = \frac{Pf}{0.95B}$$

The amount of fuel W held up outside the reactor in the total fuel cycle operations depends on the total out-of-reactor time T_o , in days. Thus,

$$W = w T_o = \frac{L T_o}{T} = \frac{Pf}{0.95} \left(\frac{T_o}{B} \right)$$

If two cases are compared wherein L , P , and f are constant,

$$\frac{W_2}{W_1} = \left(\frac{T_o}{T} \right)_2 / \left(\frac{T_o}{T} \right)_1 = \left(\frac{T_o}{B} \right)_2 / \left(\frac{T_o}{B} \right)_1$$

For a reactor with a given irradiation time T , the size of the out-of-reactor fuel inventory is directly proportional to T_o , the out-of-reactor fuel cycle time. Thus, while lower burnup results in a larger amount of fuel inventory, other things being equal, a shorter out-of-reactor fuel cycle time compensates by lowering the inventory amount. Thus, as an illustration, fuel inventory (and hence the charges) will be the same for the following cases:

	Case 1	Case 2	Case 3
Burnup, %	3	5	10
Time out of reactor, days	72	120	240

Inventory charges are influenced by reactor parameters (especially power density and fuel management schedules) even more than by variants of processing, and the longer cooling time for aqueous than for the nonaqueous processes results in a penalty for aqueous processes that is especially pronounced for the 180-day reactor fueling cycle time on which TABLE IX-6 was based.

ADDENDUM

Publications

by

Chemical Engineering Division Personnel

(From January 1, 1964, to April 30, 1965)

A. Open-Literature Publications

Bennett, G. A., L. Burris, Jr., and R. C. Vogel

Extraction of Fission Products from Molten Uranium-Plutonium
Alloys by Halide SaltsAbstracts of Papers presented at Am. Chem. Soc. Meeting,
Chicago, Aug. 30-Sept. 4, 1964, p. 18-R. Abstract.

Brugger, J. E., F. F. Rieke, and R. A. Semmler

Engine-Wear Studies with Radioisotopes*
Isotopes and Radiation Technology 1, 256 (1964).Burris, L., Jr., K. M. Harmon, G. E. Brand, E. W. Murbach, and R. K.
Steunenbergh

Pyrometallurgical and Pyrochemical Fuel Processing

Presented at the Third Intern. Conf. on the Peaceful uses of Atomic
Energy, Geneva, Aug. 31-Sept. 9, 1964, paper A/CONF. 28/P/251

Cafasso, F. A., H. M. Feder, and I. Johnson

Partition of Solutes Between Liquid Metals. II. The Lead-Zinc System
J. Phys. Chem. 68, 1944-8 (July 1964).

Cairns, E. J. and A. D. Tevebaugh

CHO Gas Phase Compositions in Equilibrium with Carbon, and Carbon
Deposition Boundaries at One Atmosphere*J. Chem. Eng. Data 9(3): 453 (July 1964).

Chandrasekharaiah, M. S.

Dissociation Energies of Alkaline-earth Oxides*
J. Phys. Chem. 68, 2020 (July 1964).

Chasanov, M. G., I. Johnson, and R. V. Schablaske

The System Zinc-Technetium-99

J. Less-Common Metals 7, 127-132 (1964).

* Work performed prior to joining Chemical Engineering Division.

Chemical Engineering Division

Development of Processes for Nuclear Fuel Recovery.

Part I. Pyrometallurgical Processes

Argonne National Laboratory Reviews 1(4), 3-6 (October 1964).

Chemical Engineering Division

Development of Processes for Nuclear Fuel Recovery.

Part II. Fluoride Volatility Processes

Argonne National Laboratory Reviews 2(1), 6-10 (January 1965).

Crouthamel, C. E., D. C. Stupedia, C. M. Stevens, and P. Kafalas

Capture to Fission Ratios of U^{233} , U^{235} , U^{238} , and Pu^{239} in
EBR-I, Mark IIINucl. Sci. Eng. 21(2), 179-185 (February 1965).

Elder, J. P. and G. Wranglen

Mass Transfer at Plane Plate Electrodes*

Electrochem. Tech. 2, 34 (January-February 1964).

Elder, J. P.

Mass Transfer at Vertically Disposed Plane Plate Electrodes.*

J. Electrochem. Soc. 111, 191C (August 1964). Abstract.

Foster, M. S., C. E. Crouthamel, D. M. Gruen, and R. L. McBeth

First Observation of a Solution of Li_3Bi , and Intermetallic in Molten
Lithium Chloride and Lithium Chloride-Lithium FluorideJ. Phys. Chem. 68, 980 (April 1964). Note.

Foster, M. S., S. E. Wood, and C. E. Crouthamel

Thermodynamics of Binary Alloys. I. The Lithium-Bismuth System**

Inorg. Chem. 3(10), 1428 (October 1964).

Gabor, J. D.

Lateral Solids Mixing in Fluidized-Packed Beds

A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 10(3), 345 (May 1964).

Gabor, J. D.

Fluidizing Gas Velocities

Chem. Process. (Chicago) 27(17), 86 (December 1964). Nomograph.

Gabor, J. D. and W. J. Mecham

Radial Gas Mixing in Fluidized-Packed Beds***

Ind. Eng. Chem. Fundamentals 3(1), 60 (February 1964).

* Work performed prior to joining Chemical Engineering Division.

** Also published as an ACS abstract.

*** Also listed in ANL-6875.

- Gabor, J. D., W. J. Mecham, and A. A. Jonke
Heat Transfer in Fluidized-Packed Beds as Applied to the Fluorination of Uranium Dioxide Pellets
Chem. Eng. Progr. Symp. Ser. Nuclear Engineering, Part X, 60 (47), 96 (1964).
- Gabor, J. D.
Lateral Transport in a Fluidized-Packed Bed: Part I. Solids Mixing
A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 11(1), 127-129 (January 1965).
- Gabor, J. D., B. E. Stangeland, and W. J. Mecham
Lateral Transport in a Fluidized-Packed Bed: Part II. Heat Transfer
A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 11(1), 130-132 (January 1965)
- Greenberg, E., C. A. Natke, and W. N. Hubbard
The Heat of Formation of Silicon Carbide by Fluorine Bomb Calorimetry
Abstracts of Papers presented at Am. Chem. Soc. Meeting, Chicago, Aug. 30-Sept. 4, 1964, p. 51-V. Abstract.
- Gruen, D. M., R. L. McBeth, M. S. Foster, and C. E. Crouthamel
Absorption Spectra of Alkali Metal Tellurides in Molten Alkali Halides
Abstracts of Papers presented at Am. Chem. Soc. Meeting, Chicago, Aug. 30-Sept. 4, 1964, p. 41-0. Abstract.
- Holmes, J. T. and J. J. Barghusen
Pilot Plant Development of a Fluid-Bed Fluoride Volatility Process for High Enriched Uranium-Alloy Fuels
Abstracts of Papers presented at Am. Chem. Soc. Meeting, Chicago, Aug. 30-Sept. 4, 1964, p. 21-R. Abstract.
- Hootman, H. E., J. C. Hesson, and L. Burris, Jr.
Diffusivity of Uranium in Various Liquid Metal Solutions
J. Electrochem. Soc. 111, 199C (August 1964). Abstract.
- Hubbard, W. N.
Calorimetry
Science 147, 312-314 (Jan. 15, 1965).
- Johnson, C. E., C. E. Crouthamel, and S. E. Wood
Anomalous and Nonequilibrium Breaks in Fused Salt Thermal Analysis Curves
Nature 201, 293 (Jan. 18, 1964).

- Johnson, C. E., S. E. Wood, and C. E. Crouthamel
Studies of Lithium Hydride Systems. I. Solid-Liquid Equilibrium in
the Lithium Chloride-Lithium Hydride System*,**
Inorg. Chem. 3, 1487 (November 1964).
- Johnson, G. K., E. Greenberg, J. L. Margrave, and W. N. Hubbard
The Heats of Formation of the Diborides of Zirconium, Hafnium, and
Tantalum by Fluorine Bomb Calorimetry
Abstracts of Papers, 19th Calorimetry Conference,
October 13-16, 1964. Abstract.
- Johnson, I.
Thermodynamics of Plutonium, Thorium and Uranium Metallic Systems
Proceedings of International Symposium on Compounds of Interest
in Nuclear Reactor Technology, Nuclear Metallurgy, Vol. 10,
Met. Soc. AIME, New York, 1964, pp. 171-192.
- Johnson, I., R. V. Schablaske, B. S. Tani, and K. E. Anderson
CeCd₆-Type Rare Earth-Cadmium Alloys
Trans. Met. Soc. AIME 230, 1485 (October 1964).
- Johnson, I. and M. G. Chasanov
Thermodynamics of the Plutonium-Zinc System
J. Inorg. Nucl. Chem. 26, 2059-2067 (1964).
- Johnson, T. R., G. D. White, O. L. Kruger, R. K. Steunenberg, and J. H.
Handwerk
Uranium and Plutonium Carbide Developments at Argonne National
Laboratory
Proc. 4th Uranium Carbide Meeting, East Hartford, Conn., May 1963
TID-7676, pp. 1-9.
- Kilpatrick, M. and S. K. Lott
Reaction of Flowing Steam with Refractory Metals. I. Molybdenum
1100-1700°C
Abstracts of Papers presented at Am. Chem. Soc. Meeting, Chicago,
Aug. 30-Sept. 4, 1964, p. 14-V. Abstract.
- Knudsen, I. E., H. E. Hootman, and N. M. Levitz
A Fluid-bed Process for the Direct Conversion of Uranium Hexafluoride
to Uranium Dioxide
Nucl. Sci. Eng. 20, 259-265 (November 1964).

* Also listed in ANL-6875.

** ACS Abstract, presented at ACS Meeting, Phil., Pa., April 1964.

- Kybett, B. D., C. K. Barker, G. K. Johnson, and J. L. Margrave
 The Heats of Formation of C_3O_2 , Se_4N_4 and of the Various Crystalline
 Forms of TiO_2 by Combustion Calorimetry*
 Abstracts of Papers, 19th Calorimetry Conference, Oct. 13-16, 1964.
 Abstract.
- Kyle, M. L., P. A. Nelson, and L. Burris, Jr.
 Corrosion of Steel and Tantalum by Molten Cadmium-Magnesium-Zinc
 Solutions
 J. Electrochem. Soc. 111, 199C (August 1964). Abstract.
- Lawroski, S. et al.
 Reactor Fuel Process. 6(4), (Fall 1963)**
 Reactor Fuel Process. 7(1), (Winter 1963-64)
 Reactor Fuel Process. 7(2), (Spring 1964)
 Reactor Fuel Process. 7(3), (Summer 1964).
 Reactor Fuel Process. 7(4), (Fall 1964).
- Lawroski, S. and L. Burris, Jr.
 Processing of Fuel Materials by Pyrometallurgical Methods
 Atomic Energy Review, 2(3), 3 (November 1964).
- Levenson, M., C. E. Stevenson, and J. C. Hesson
 Safety Aspects of the EBR-II Reprocessing Facility
 Presented at the Third Intern. Conf. on the Peaceful Uses of Atomic
 Energy, Geneva, Aug. 31-Sept. 9, 1964, paper A/CONF.28/P/280.
- Levitz, N. M., J. J. Barghusen, J. T. Holmes, and A. A. Jonke
 Halogenation Studies on Nuclear-Fuel-Element Materials in a Two-
 Zone Fluid-Bed Reactor
 Chem. Eng. Progr. Symp. Ser. Nuclear Engineering, Part X,
60(47), 84 (1964).
- Leibowitz, L., J. D. Bingle, and M. Homa
 An X-ray Study of Oxidized Uranium Surfaces**
 J. Electrochem. Soc. 111, 248 (February 1964).
- Liimatainen, R. C. and P. Jauho
 Finland's Atomic Energy Program**
 ANS Nuc. News 7(3), 3 (1964).

* Work performed prior to joining Chemical Engineering Division.

** Also listed in ANL-6875.

Liimatainen, R. C.

Nuclear Reactor Safety: Meltdown of Metals at High Temperatures and Metal-Water Reactions (in Finnish)*
J. Finnish Phys. Soc. No. 1, 27 (1964)

Liimatainen, R. C., L. Baker, Jr., R. O. Ivins, F. J. Testa, J. F. Boland, and H. Lawroski

Studies on the Meltdown in Water of Oxide Core, Zircaloy-2 Clad Fuel in TREAT
Trans. Am. Nucl. Soc. 7, 448 (November 1964). Abstract.

Liimatainen, R. C. and B. S. Swanson

Vapor-Liquid Equilibrium in the System Bromine Pentafluoride-Uranium Hexafluoride
A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 10 (6), 860 (November 1964).

Littman, H.

Solids Mixing in Straight and Tapered Fluidized Beds
A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 10 (6), 924 (November 1964).

Luner, C. and M. V. Murray

Factors Affecting the Morphology and Growth of FeSn_2 **
J. Electrochem. Soc. 111, 407 (1964).

Mecham, W. J., J. D. Gabor, and A. A. Jonke

Pilot Plant Studies of a Direct Fluorination Process Applied to Uranium Dioxide Reactor Fuels
Chem. Eng. Progr. Symp. Ser. Nuclear Engineering, Part X, 60 (47), 76 (1964).

Meyer, R. J., R. F. Oldham, and R. P. Larsen

Separation and Spectrophotometric Determination of Technetium in Fission Anal. Chem. 36, 1975 (September 1964).

Moriarty, J. L., I. Johnson, and H. M. Feder

The Role of Coprecipitation in Alloy Partition During the Crystallization of Ternary Systems
Trans. Met. Soc. AIME 230, 777 (June 1964).

* Listed in ANL-6875 as "Nuclear Reactor Safety: The High Temperature Reactions of Molten Metals with Water." Work performed at Finland Institute of Technology.

** Work performed prior to joining Chemical Engineering Division.

- Nelson, P. A., M. L. Kyle, G. A. Bennett, and L. Burris, Jr.
Corrosion of Refractory Metals by Zinc-Magnesium-Uranium and Halide Salt Systems
J. Electrochem. Soc. 111, 200C (August 1964). Abstract.
- Pierce, R. D. and L. Burris, Jr.
Pyroprocessing of Reactor Fuels
Selected Reviews in Reactor Technology - 1964,
L. E. Link, ed., TID-8540, pp. 411-476.
- Ramaswami, D., N. M. Levitz, and A. A. Jonke
Bench-scale Development of a Fluid-bed Fluoride Volatility Process for High-Enriched Uranium-Alloy Fuels
Abstracts of Papers presented at Am. Chem. Soc. Meeting, Chicago, Aug. 30-Sept. 4, 1964, p. 20-R. Abstract.
- Rudzitis, E., H. M. Feder, and W. N. Hubbard
Fluorine Combustion Technique for Metals Forming Nonvolatile (Ionic) Fluorides
Abstracts of Papers, 19th Annual Calorimetry Conference, October 13-16, 1964. Abstract.
- Rudzitis, E., R. Terry, H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. VIII. The Enthalpy of Formation of Zinc Difluoride
J. Phys. Chem. 68, 617-619 (1964).
- Rudzitis, E., H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. IX. The Enthalpy of Formation of Magnesium Difluoride
J. Phys. Chem. 68, 2978 (October 1964).
- Schablaske, R. V., B. S. Tani, and M. Chasanov
The Crystal Structure of ScCd_3 *
Trans. Met. Soc. AIME 230, 248 (February 1964).
- Schneider, A. and Ju Chin Chu
Kinetics of Sulfochlorination of Cyclohexane in Carbon Tetrachloride Induced by Gamma Radiation**
A.I.Ch.E. (Am. Inst. Chem. Engrs.) J. 10 (6), 930 (November 1964)

* Also listed in ANL-6875.

** Work performed prior to joining Chemical Engineering Division.

Seefeldt, W. B.

Corrosion and Materials of Construction in Chemical Processing of Reactor Fuels
Progress in Nuclear Energy, Series IV, Vol. V, C. M. Nicholls, Ed., Pergamon Press, New York, 1963, pp. 409-446.

Semmler, R. A., J. E. Brugger, and F. F. Rieke

Application of Gamma Scattering to the Measurement of Bulk Density* in Progress in Applied Materials Research, Vol. 6, E. G. Stanford, J. H. Fearon, and W. J. McGonnagle, Eds., Heywood Scientific Books (Temple Press), London, 1964, pp. 263-309.

Steindler, M. J. and W. H. Gunther

The Absorption Spectrum of Plutonium Hexafluoride
Spectrochim. Acta 20, 1319-1322 (1964). Research Note.

Steindler, M. J., D. V. Steidl, and J. Fischer

The Decomposition of Plutonium Hexafluoride by Gamma Radiation
J. Inorg. Nucl. Chem. 26, 1869-1878 (1964).

Swift, D. L. and S. K. Friedlander

The Coagulation of Hydrolysols by Brownian Motion and Laminar Shear Flow*
J. Colloid Sci. 19, 621-647 (September 1964).

Sympson, R. F., R. P. Larsen, R. J. Meyer and R. D. Oldham

Amperometric Titration of Uranium (IV) with Iron (III)
Anal. Chem. 37, 58-60 (January 1965).

Tetenbaum, M.

Compounds of Interest, a meeting report on International Symposium on Compounds of Interest in Nuclear Technology, University of Colorado, Aug. 3-5, 1964.
Nucl. News 7 (12), 24-28 (December 1964).

Tetenbaum, M.

Thermoelectric Properties of Uranium Monosulfide, Thorium Monosulfide, and US-ThS Solid Solutions**
J. Appl. Phys. 35 (8), 2468 (August 1964).

Tevebaugh, A. D.

Phosphinoarylboranes*
Inorg. Chem. 3, 302 (1964).

* Work performed prior to joining Chemical Engineering Division.

** Also listed in ANL-6875.

- Tevebaugh, A. D. and E. J. Cairns
The Triple Point Temperature of Tellurium*
J. Chem. Eng. Data 9 (2), 172 (1964).
- Trice, V. G. and R. K. Steunenberg
Small-scale Demonstration of the Melt Refining of Highly Irradiated
EBR-II Uranium-Fissium Fuel
Abstracts of Papers presented at Am. Chem. Soc. Meeting,
Chicago, Aug. 30-Sept. 4, 1964, p. 17-R. Abstract.
- Veleckis, E. and I. Johnson
Decomposition Pressure of $TcZn_6$
J. Phys. Chem. 68, 1257 (May 1964). Note.
- Vinogradov, S. N. and M. Kilpatrick
Association of N-H Compounds. II. Infrared Spectroscopic Investigation
of the Self-Association of 3,5-Dimethylpyrazole in Benzene and in
Carbon Tetrachloride*,**
J. Phys. Chem. 68, 181 (1964).
- Vogel, G. J., E. L. Carls, N. M. Levitz, and W. J. Mecham
A Pilot Plant for Fluid-Bed Fluoride Volatility Processing of Uranium
Dioxide-Plutonium Dioxide Reactor Fuels
Trans. Am. Nucl. Soc. 7, 396 (November 1964). Abstract.
- Vogel, R. C.
Fuel Reprocessing
Nucl. News 7, 90 (October 1964).
- Vogel, R. C., W. H. Carr, G. I. Cathers, J. Fischer, L. P. Hatch, R. W.
Horton, A. A. Jonke, R. P. Milford, J. J. Reilly, and G. Strickland
Fluoride Volatility Processes for the Recovery of Fissionable
Material from Irradiated Reactor Fuels
Presented at the Third Intern. Conf. on the Peaceful Uses of Atomic
Energy, Geneva, Aug. 31-Sept. 9, 1964, paper A/CONF.28/P/250.
- Wenz, D. A., M. D. Adams, and R. K. Steunenberg
Formation and Spectra of Uranyl (V) Chloride in Molten Chloride Solvents
Inorg. Chem. 3, 989-992 (July 1964).

* Work performed prior to joining Chemical Engineering Division.

** Also listed in ANL-6875.

Young, T. F., Y. C. Wu, and W. L. Groenier

Thermochemistry of Dilute Aqueous Sulfuric Acid. Comparison of Theory and Experiment at 25°C.*

Abstracts of Papers, 19th Calorimetry Conference, October 13-16, 1964. Abstract.

Ziegler, E. N. and W. T. Brazelton

Mechanism of Heat Transfer to a Fixed Surface in a Fluidized Bed
Ind. Eng. Chem. Fundamentals 3 (2), 94 (May 1964).

Ziegler, E. N., L. B. Koppel, and W. T. Brazelton

Effects of Solid Thermal Properties on Heat Transfer to Gas Fluidized Beds

Ind. Eng. Chem. Fundamentals 3 (4), 324-328 (November 1964).

B. Papers Accepted for Publication in the Open Literature

Anastasia, L. J. and W. J. Mecham

Oxidation-Fluorination of Uranium Dioxide Pellets in a Fluidized Bed
Accepted for publication in Ind. Eng. Chem., Process Design Develop.

Baker, L., Jr. and R. C. Liimatainen

Chemical Reactions

Accepted for publication as Chapter 17 of Technology of Nuclear Reactor Safety, Vol. 2, to be published by MIT Press for the AEC.

Baker, L., Jr.

Metal-Water Reactions

Accepted for publication as a section of Chapter 4 (Chemical Reactions) of the Oak Ridge Reactor Containment Handbook.

Bennett, G. A., P. A. Nelson, and L. Burris, Jr.

Corrosion of Stainless Steels by Zinc Vapor

Accepted for publication in Trans. Met. Soc. AIME.

Chasanov, M. G., P. A. Nelson, and A. D. Tevebaugh

Wetting of UN and Other Uranium Ceramics by Molten Sodium
(letter to the editor)

Accepted for publication in J. Nucl. Mater.

* Work performed at University of Chicago and Argonne National Laboratory

Greenberg, E., C. Natke, and W. N. Hubbard

Fluorine Bomb Calorimetry: X. The Enthalpies of Formation of Niobium and Tantalum Pentafluorides

Accepted for publication in J. Phys. Chem.

Hesson, J. C., H. E. Hootman, and L. Burris, Jr.

Diffusivity of Uranium in Various Liquid Metals

Accepted for publication in Electroch. Tech.

Holmes, J. T. and M. G. Baerns

Evaluation of Physical Properties of Gases and Multicomponent Gas Mixtures

Accepted for publication in Chem. Eng.

Holmes, J. T.

Simplified Technique for Using the Diaphragm Type, Liquid Diffusion Cell

Accepted for publication in Rev. Sci. Instr.

Irish, D. E. and T. F. Young

The Raman Spectrum of Molten-Zinc Chloride*

Accepted for publication in J. Chem. Phys.

Jonke, A. A.

Reprocessing of Nuclear Reactor Fuels by Processes Based on Volatilization, Fractional Distillation and Selective Adsorption

Accepted for publication in the Atomic Energy Review (International Atomic Energy Agency).

Kilpatrick, M. and S. K. Lott

Reaction of Flowing Steam with the Refractory Metals Niobium and Tantalum

Accepted for publication in J. Less-Common Metals.

Kilpatrick, M. and S. K. Lott

Reaction of Flowing Steam with Refractory Metals: I. Molybdenum (1100-1700°C)**

Accepted for publication in J. Phys. Chem.

Knighton, J. B. and R. K. Steunenberg

Distribution of Transuranium Elements between Magnesium Chloride and Zinc-Magnesium Alloy

Accepted for publication in J. Inorg. Nucl. Chem.

* Work performed prior to joining Chemical Engineering Division.

** Listed elsewhere as an abstract of a paper presented at an ACS meeting.

- Liimatainen, R. C., R. O. Ivins, and F. J. Testa
Experimental Studies in Nuclear Reactor Safety: The Reaction of Uranium and a Uranium Alloy with Water as Initiated by a Meltdown during a Power Excursion in TREAT
Accepted for publication in Trans. Am. Nucl. Soc.
- Liimatainen, R. C., R. O. Ivins, and F. J. Testa
Metal-Water Reactions Initiated by a Short-Period Nuclear Reactor Excursion (Kiwi-TNT)
Accepted for publication in Trans. Am. Nucl. Soc.
- Nelson, P. A., D. K. Butler, M. G. Chasanov, and D. Meneghetti
Fuel Properties and Nuclear Performance of Fast Reactors Fueled with Molten Chlorides (Abstract)
Accepted for publication in Trans. Am. Nucl. Soc.
- Rudzitis, E., H. M. Feder, and W. N. Hubbard
Fluorine Bomb Calorimetry. XI. Enthalpy of Formation of Yttrium Trifluoride
Accepted for publication in J. Phys. Chem.
- Schnizlein, J. G., J. Brewer, and D. F. Fischer
Temperature Transducer for Thermogravimetric Studies
Accepted for publication in Rev. Sci. Instr.
- Walsh, W. J. and G. Burnet
Metal Distillation Surface Measurements with an X-Ray Spectrometer*
Accepted for publication in Trans. Am. Nucl. Soc.
- Wilson, R. E. and C. Barnes, Jr.,
Metal-Steam Reactions at High Temperatures,
Accepted for publication in Trans. Am. Nucl. Soc.
- Wu, Y. C., M. B. Smith, and T. F. Young
Heats of Mixing of Electrolytes Having Common Ions**
Accepted for publication in J. Phys. Chem.
- Wu, Y. C., M. B. Smith, and T. F. Young
Heats of Mixing of Electrolytes of the 1-1 Charge Type**
Accepted for publication in J. Phys. Chem.

* Work performed prior to joining Chemical Engineering Division.

** Work performed at University of Chicago and Argonne National Laboratory.

C. ANL Reports

Bennett, G. A., L. Burris, Jr., and R. C. Vogel
Halide Slagging of Uranium-Plutonium Alloys
ANL-6918.

Bernstein, G. J., A. A. Chilenskas, and R. F. Malecha
Interbuilding Fuel Transfer Coffin for the EBR-II Reactor
ANL-6934.

Burris, L., Jr., I. G. Dillon, and R. K. Steunenberg
The EBR-II Skull Reclamation Process, Part I. General Process
Description and Performance
ANL-6818.

Chang, K. S., R. G. Akins, L. Burris, Jr., and S. G. Bankoff
Free Convection of a Low Prandtl Number Fluid in Contact with a
Uniformly Heated Vertical Plate
ANL-6835.

Chelley, N. R., C. C. Honesty, and R. K. Steunenberg
Laboratory Studies of Iodine Behavior in the EBR-II Melt
Refining Process
ANL-6815.

Foster, M. S., C. E. Johnson, A. K. Fischer, and C. E. Crouthamel
AMU-ANL Conference on Direct Energy Conversion, November 4-5, 1963.
ANL-6802, pp. 53-63.

Graae, J. E. A.
Design of a Remotely Removable and Replaceable Crane-Bridge Drive
Unit for the EBR-II Fuel Cycle Facility
ANL-6966.

Hesson, J. C. and L. Burris, Jr.
Nuclear Criticality Control in the EBR-II Fuel Cycle Facility
ANL-6831.

Holmes, J. T. and M. G. Baerns
Evaluation of Physical Properties of Gases and Multicomponent Gas
Mixtures
ANL-6951.

Jarry, R. L., A. V. Hariharan, G. Manevy, J. Fischer, J. J. Stockbar,
J. G. Riha, T. D. Baker, and G. W. Redding
Laboratory Investigations in Support of Fluid Bed Fluoride Volatility
Processes: Part IV. The Fluid Bed Fluorination of U_3O_8
ANL-6763.

Johnson, T. R., R. D. Pierce, L. Burris, Jr., and R. K. Steunenberg
The EBR-II Skull Reclamation Process. Part II. Skull Oxidation
ANL-6874.

Knudsen, I. E., N. M. Levitz, and A. A. Jonke
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 6. Preparation of Dense Uranium Dioxide Particles from Uranium
Hexafluoride in a Fluidized Bed
ANL-6902.

Ramaswami, D., N. M. Levitz, J. T. Holmes, and A. A. Jonke
Engineering Development of Fluid-Bed Fluoride Volatility Processes.
Part 1. Bench-scale Investigation of a Process for Zirconium-Uranium
Alloy Fuel
ANL-6829.

Steindler, M. J. and W. H. Gunther
Laboratory Investigations in Support of Fluid Bed Fluoride Volatility
Processes. Part VI. A. The Absorption Spectrum of Plutonium
Hexafluoride. B. Analysis of Mixtures of Plutonium Hexafluoride and
Uranium Hexafluoride by Absorption Spectrometry.
ANL-6817.

Sutherland, K. S.
The Effect of Particle Size on the Properties of Gas-Fluidized Beds
ANL-6907.

Tetenbaum, M.
Thermoelectric Parameter Studies on US, ThS and US-ThS Solid Solutions
A Seminar on Groups V and VI Anions held at Argonne National
Laboratory, February 26 and 27, 1964, ed. R. J. Beals, J. H. Handwerk,
and J. F. Schumar
ANL-6856, pp. 48-52.

Vogel, R. C., M. Levenson, and V. H. Munnecke
Chemical Engineering Division Semiannual Report, July-December 1963
ANL-6800.

Vogel, R. C., M. Levenson, and V. H. Munnecke
Chemical Engineering Division Research Highlights, May 1963-April 1964.
ANL-6875.

Vogel, R. C., M. Levenson, and F. R. Masten
Chemical Engineering Division Summary Report, January-June 1964
ANL-6900.

Ziegler, E. N.

Heat and Mass Transfer to a Gas-Fluidized Bed of Solid Particles
ANL-6807.

D. Papers Presented at Scientific Meetings

Baker, L., Jr. and R. O. Ivins

A Calculation Demonstrating the Effect of the Zirconium-Water
Reaction on the Analysis of a Loss-of-Coolant Accident
Presented at Int. Symp. on Fission Product Release and Transport
under Accident Conditions, Oak Ridge, April 5-7, 1965.

Burris, L., Jr.

EBR-II Fuel Processes
Presented at Chemical Technology Division, Oak Ridge National
Laboratory, Dec. 15, 1964.

Carls, E. L., G. J. Vogel, N. M. Levitz, and W. J. Mechem

A Pilot Plant for Fluid-Bed Fluoride Volatility Processing of Uranium
Dioxide-Plutonium Dioxide Reactor Fuels
Presented at American Nuclear Society Meeting, San Francisco,
Nov. 30-Dec. 3, 1964.

Crouthamel, C. E.

Properties of Intermetallic Compounds and Fused Salt Solutions
Presented at Metallurgy and Chemical Eng. Dept. Purdue Univ.,
Oct. 14, 1964.

Ebersole, E. R., R. P. Larsen, M. T. Laug, and J. J. McCown

Lanthanum-139 as a Burnup Monitor - A Mass Spectrometric Method
Presented at Eighth Conference on Analytical Chemistry in Nuclear
Reactor Technology, Gatlinburg, Tenn., October 1964.

Fischer, A. K.

Some Experimental Aspects of Mutual Solubility in Fused Systems of
Alkali Metals and their Halides*
Presented at Chemistry Department, Northwestern University,
Evanston, Ill., March 5, 1964.

Foster, M.

Regenerative Cell Systems*
Presented at Mechanical Engineering Dept., University of Minnesota,
January 16, 1964.

* Also listed in ANL-6875.

Gabor, J. D.

Fluidized-Packed Beds

Presented at A.I.Ch.E. Meeting, Boston, Dec. 6-10, 1964.

Hesson, J. C.

Thermodynamics and Thermal Efficiencies of Thermally Regenerative
Emf Cell Systems

Presented at ACS Meeting, Detroit, April 8, 1965.

Hubbard, W. N.

Calorimetry*

Presented at a joint seminar for Baker University and the University
of Kansas, Feb. 7, 1964. y

Johnson, I.

Chemistry of Liquid Metal Solutions*

Presented at University of Minnesota, March 12, 1964.

Johnson, I.

Partition of Metals between Liquid Metal Solutions and Fused Salts

Presented at Conference on "Applications of Fundamental Thermo-
dynamics to Metallurgical Processes," University of Pittsburgh,
Nov. 30, 1964.

Larsen, R. P.

The Determination of Fuel Burnup in Nuclear Reactors

Presented at Ohio University, May 1964.

Larsen, R. P., R. J. Meyer, M. T. Laug, and G. W. Smith

Uranium-235 Thermal Fission Yields of Cesium-133 and -137

Presented at Eighth Conference on Analytical Chemistry in Nuclear
Reactor Technology, Gatlinburg, Tenn., October 1964.

Liimatainen, R. C.

Some Aspects of Education and Atomic Energy in Finland,

Presented at Founder's Day convocation of Suomi College, Hancock,
Mich., March 17, 1965.

Meyer, R. J., R. D. Oldham, R. J. Popek, and R. P. Larsen

Technetium as a Burnup Monitor for Fast and Thermal Reactors

Presented at Eighth Conference on Analytical Chemistry in Nuclear
Reactor Technology, Gatlinburg, Tenn., October 1964.

* Also listed in ANL-6875.

Steunenberg, R. K.

Pyrometallurgical Processing of Uranium-Plutonium Fuel Alloy
Presented at Chemical Technology Division, ORNL, Feb. 16, 1965.

Young, T. F.

A Modified Principle of Ionic Strength
Presented at Chemical Physics Seminar, Bell Telephone Laboratories,
Murray Hill, New Jersey, Feb. 24, 1964.

Young, T. F.

Interactions Between Simple Ions
Presented at Laboratory Chemistry Colloquium, Oak Ridge National
Laboratory, June 15, 1964.