ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

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Stephen Lawroski, Division Director
W. A. Rodger, Associate Division Director
R. C. Vogel, Associate Division Director
V. H. Munnecke, Assistant Division Director

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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT
January, February, and March, 1958

SUMMARY

I. Fluoride Volatilization Separations Process (pages 16 to 29)

Development work was continued on the fused fluoride process for the recovery of enriched uranium from zirconium-matrix fuel alloys. The alloy is dissolved by immersing it in molten sodium fluoride-zirconium fluoride at 600°C and passing hydrogen fluoride vapor through the system. The dissolved uranium tetrafluoride in the melt is then volatilised as uranium hexafluoride by sparging with fluorine. The uranium hexafluoride product is purified and decontaminated by fractional distillation.

Additional corrosion tests were made on a variety of metals in an effort to find a material of construction suitable for the fluorination step. All the metals tested, with the exception of Hastelloy B, were attacked rapidly in the fluorinated melt. The attack was particularly severe at the melt-gas interface when tests were made with partially submerged specimens of the metals.

Further studies were made on the permeation of a six-inch graphite crucible by molten sodium fluoride-zirconium fluoride. Analytical data obtained from sections of the crucible indicated that about one-third of the voids in the graphite were filled after 144 hours exposure to the fused salt under 1000 mm pressure. Uranium (as the tetrafluoride) was added to the melt after 24 hours exposure of the crucible to the melt alone. Analyses of the crucible showed a decreasing uranium concentration toward the outside of the crucible wall. The fused salt concentration in the graphite and the uranium concentration in the salt both increased with longer exposure times.

Carrier-free tracer experiments were performed on the behavior of niobium and ruthenium in the fused fluoride process. Niobium was removed effectively from a hydrogen fluoride stream by a sodium fluoride trap. Earlier results which indicated that ruthenium is not volatilised from molten sodium fluoride-zirconium fluoride by fluorine sparging were confirmed with tracer ruthenium.

Pilot plant operations were directed toward development of two operations basic to fluoride volatility processes, namely, the fused fluoride dissolution of uranium-zirconium alloy fuels and the purification of uranium hexafluoride by fractional distillation.
II. Liquid Metal Fuel Reprocessing (pages 30 to 33)

A major portion of the laboratory investigation within the group has been directed towards the development of a fluoride volatility process to recover and purify the core fluid from the Liquid Metal Fuel Reactor (LMFR). Uranium-233 dissolved in bismuth (maximum uranium concentration, about 1350 ppm) is the fuel. The proposed fluoride volatility flow-sheet involves fused salt extraction of core fluid with a hydrogen fluoride sparge. This removes uranium as the tetrafluoride, plus the majority of the fission products as fluorides. The uranium tetrafluoride is converted to uranium hexafluoride and the uranium hexafluoride is purified by distillation. The uranium is then reduced to the metal, returned to the bismuth and thence to the reactor. Most of the laboratory work of the past quarter has consisted of assembling and testing new equipment.

Corrosion tests of materials of construction having potential use in the fluoride volatility process for reprocessing LMFR core fluid showed silver, gold, molybdenum and platinum to have promise when in contact with hydrofluorinated sodium fluoride-zirconium fluoride melts. The corrosion effects of the contact of bismuth and fused sodium fluoride-zirconium fluoride on molybdenum are being studied. Molybdenum appears to be very resistant to attack in this medium.

III. Fluidization Studies (pages 34 to 53)

Development work continued on the fluid-bed drying of zirconium-uranium-fluoride solutions. Efforts were concentrated on the spraying of solutions containing precipitated uranium tetrafluoride. This is an intermediate step in the proposed fluorination process for separation of uranium from high zirconium-low uranium alloys. Difficulties, such as nozzle caking and particle growth in the bed; continued over a wide range of variables. Some success in operations has been achieved at temperatures near 300 C.

Laboratory studies were made to evaluate reducing agents which will completely and quickly precipitate the uranium tetrafluoride in the feed solutions to the fluid-bed driers. Other tests are being conducted to find additives for the zirconium-uranium solutions which will increase the porosity of the solids produced and permit complete separation of the uranium during fluorination.

Work on fluid-bed calcination of waste solutions has been directed toward equipment modifications, the determination of non-volatile fission product activity in the gas, the utility of carbon monoxide in reducing ruthenium volatilization and providing internal heat generation, ignition
testing of the solid product at elevated temperatures to study fission product volatilization behavior, and a bench-scale test of a new proposal for filter blowback.

Application of a fluid-bed technique to apply a ceramic-glaze coating on calcined oxide continued. Some study has been made of the feasibility of improving the heat transfer characteristics of the oxide by compacting with powdered metal.

Qualitative mixing studies have started in straight and tapered fluidized bed columns. Mixing coefficients will be measured using a radioactive pulse-tracer technique. A mathematical analysis of the problem is presented.

A pilot plant study of the fluidized-bed fluorination of uranium tetrafluoride to uranium hexafluoride is under way. Fluidized-bed fluorination offers a means of producing uranium hexafluoride from various granular uranium-bearing materials, with advantages attendant to non-aqueous, fluidized solid-gas systems. Tests made on refined green salt showed temperature had a large effect on fluorine efficiency (maximum efficiency 91 per cent at 450 °C) while fluorine concentration had a small effect. Fluorine concentrations above 43 per cent could not be controlled due to limitations on heat removal.

IV. Reactor Chemistry (pages 54 to 67)

The efforts to clarify the factors involved in the pyrophoricity of reactor materials are proceeding satisfactorily. The effects of many additives to uranium have been studied in oxygen. Current efforts have developed a relationship between the ignition temperature and the area-to-mass ratio or specific area. An experiment has been conducted to demonstrate that a small piece of uranium (large specific area) may serve as an igniter for the bulk metal. Several gas variables are being examined. Preliminary studies in air and mixtures of nitrogen and air have shown a complex behavior which will require further study. The variable due to the unknown reactivity of nitrogen has been eliminated by studying helium-oxygen mixtures. Between 33 and 60 volume per cent helium, the ignition temperature increases uniformly from 615 to 955 °C. No ignition was observed in 80 per cent helium. The influence of moisture content on the ignition characteristics of uranium in the various atmospheres is under investigation.

Isothermal oxidation studies of uranium have been directed toward understanding the mechanism of oxidation which proceeds in two stages and attempting correlation with ignition test results.
A new procedure to test the ignition characteristics of zirconium has not yielded satisfactorily reproducible results. Another procedure using foils initially shielded by a helium atmosphere indicates probable reproducibility of 10 degrees if many samples are used to bracket the ignition temperature.

Isothermal oxidation studies of zirconium alloys are continuing. A series of experiments has been completed on Zircaloy-3 with varied heat treatments. All tests indicated no effect of the varied heat treatment on the oxidation characteristics. The oxidation prior to breakaway is only slightly faster than that for crystal bar zirconium.

A literature survey on the oxidation of plutonium metal has been completed.

A study of metal-water reactions at high temperature has begun.

A boiling water loop is being set up to investigate the effect of a fuel element failure on operation of a boiling water reactor.

V. Chemical-Metallurgical Processing (pages 68 to 125)

Studies to determine the behavior of tracer-level fission elements in the melt-refining process have continued for fuels similar to discharged EBR-II reactor fuel. Results of experiments in which irradiated uranium diluted with "fissium" alloy was melted at 1300 C indicate that: (a) the fate of iodine may be pressure dependent; (b) at low initial concentration the evolution of xenon takes place by a slow diffusional mechanism; (c) removal of europium may be less complete than for cerium or neodymium; (d) technetium behaves as a typical noble metal, while cadmium is largely removed from the ingot.

The distribution of plutonium and uranium for two melt-refining experiments employing "fissium" alloy containing 69 weight per cent uranium and 20 weight per cent plutonium, and 11 weight per cent "fissium" (see Table 17, page 75, for "fissium" composition) has been followed. Within the experimental error of analysis, the concentration ratios of plutonium and uranium in the charges and ingots remain constant. However, analysis of the skull from a single experiment shows a plutonium enrichment factor of 1.19 relative to the ingot.
A study of the coprecipitation of lanthanum by $U_2Zn_{17}$ from liquid zinc has been completed. The Doerner-Hoskins coefficient was found to be $0.42 \pm 0.05$ for all concentrations, cooling, and stirring rates studied, except under conditions leading to high supersaturation. Under the latter conditions, the coefficient is $0.57 \pm 0.05$. A similar study using ruthenium tracer is in progress.

Auxiliary studies are under way to determine the optimum container materials, method of oxidation prevention, phase-separation method, etc., for the utilization of the Pyrozinc processes in large-scale operations. Liquid uranium-zinc alloys have been successfully protected from oxidation by the addition of magnesium to the alloy and the use of a chloride flux (Dow No. 230). The use of a controlled cooling cycle has shown promise as a method of achieving pronounced segregation of $U_2Zn_{17}$ preliminary to decantation.

Experiments are in progress to determine the decontamination of irradiated uranium possible by the use of the Pyrozinc process. A study has been started to investigate the use of the Pyrozinc process in uranium production.

The electrochemical cell study of the uranium-zinc system has yielded data on the free energy of formation of $U_2Zn_{17}$. These data have been used to compute the activity and activity coefficients of the uranium in saturated solutions.

Work continues on studies of the thermochemistry of inorganic substances. Construction of an oxygen-bomb calorimeter is nearly complete. A qualitative study of reactions of various substances with fluorine has been started as the first step in the development of the field of fluorine-bomb calorimetry. Design of a high-temperature enthalpy calorimeter is continuing.

Construction of a controlled atmosphere enclosure for the reaction calorimeters and high-precision measuring instruments has been started. Apparatus has been assembled for the preparation of some calorimetric samples.

In connection with the melt refining of spent EBR-II fuel, the data on cerium removal obtained in semi-works runs to date have been correlated as the per cent cerium remaining in the melt versus time at temperature times the ratio of crucible area to charge weight. Emphasis is currently being placed on removal of zirconium from "fissium" melts. The presence of zirconium in high concentrations in "fissium" is not considered beneficial. Removal as the carbide is being further investigated, and the possibility of removal as the boride, nitride or silicide is also being explored.
Work was concluded on the trapping of metals volatilized in the melt-refining process (predominantly cesium and sodium). "Molecular Sieves" was found to have a high capacity for cesium at 600 and 800 °C (30 and 60 weight per cent, respectively), with retention at these temperatures being essentially complete on evacuation to a few millimeters of mercury pressure. Equipment and procedures suitable for plant operation were developed and demonstrated.

In studies on the magnesium extraction of plutonium from uranium, some apparent loss of plutonium from magnesium solutions held in tantalum has occurred. Since tantalum is felt to be a suitable container material, the reasons for this loss are being investigated.

In order to operate well below the boiling point of magnesium, the uranium alloy from which plutonium is extracted is a 5 weight per cent chromium-uranium alloy. The extraction of chromium, although small, results in contamination of the plutonium product. Therefore, the chromium solubility as a function of temperature was measured down to 675 °C, where it was very low (about 0.02 weight per cent). Methods of chromium separation based on this low solubility have been postulated, and calculations have been made of chromium build-up in fuel material for various conditions of operation. A possible scheme whereby the chromium problem may be avoided by employing zinc dissolution of the blanket uranium is also presented.

Work on the Pyrozinc Process was continued by measuring the liquid phase concentrations of "fissium" constituents in zinc and zinc-6 weight per cent magnesium alloys as a function of temperature and cooling rate (see pages 111 and 112). These data indicate the extent of uranium-fission product separation which is possible. Work was also continued on separation of liquid and solid phases, and was started on the recovery of uranium from the uranium-zinc intermetallic compound.

In design and component testing for the EBR-II reprocessing facility several changes have been made in the building design. The air cell of the fuel process building was lengthened to include the disassembly operation. Cooled storage spaces were designed for storage of ingots, slags, or subassemblies. The transfer lock design will be revised. The laboratory and service building has been approved by ANL.

Designs are complete for both types of manipulators, cranes, and their removal device. Tests of electrical brushes in a dry argon atmosphere show a high rate of wear for motor use but a low rate of wear for feed rail use.
The Junior Cave windows are out for bids. The large window and shutter designs are complete. The effect of intense irradiation upon light transmittance and internal temperatures has been estimated.

A 60 degree circular sector of the argon cell has been mocked-up with a prototype window and a circular track for an operating manipulator.

Tests of crucible thermal stability are being made.

Standard 5-gallon containers will be tested for use with dry radioactive wastes. The use of vermiculite for liquid waste is being investigated as is the use of paraffin as a container sealer.

VI. Analytical Research and Services (pages 126 to 131)

A method has been devised for the determination of 0.001 per cent sulfate in uranium trioxide. Sulfur trioxide liberated on ignition with vanadium pentoxide is reduced over hot copper to sulfur dioxide, which is absorbed and determined spectrophotometrically.

The selective dissolution of uranium from LMFR samples has been accomplished by first amalgamating the bismuth and then leaching the uranium with 4 M hydrochloric acid-1 M hydrofluoric acid. It is expected that a similar procedure can be used for magnesium and zirconium.

An X-ray spectrochemical analysis for molybdenum and uranium in uranium-"fissium" alloys has been developed.

VII. Routine Operations (page 132)

The operation of the radioactive liquid waste-processing facility and the gamma-irradiation facility continued without incident.
I. **FLUORIDE VOLATILIZATION SEPARATIONS PROCESS**

Development work was continued on the fused fluoride process for the recovery of enriched uranium from zirconium-matrix fuel alloys. The alloy is dissolved by immersing it in molten sodium fluoride-zirconium fluoride at 600 °C and passing hydrogen fluoride vapor through the system. The dissolved uranium tetrafluoride in the melt is then volatilized as uranium hexafluoride by sparging with fluorine. The uranium hexafluoride product is purified and decontaminated by fractional distillation.

Additional corrosion tests were made on a variety of metals in an effort to find a material of construction suitable for the fluorination step. All the metals tested, with the exception of Hastelloy B, were attacked rapidly in the fluorinated melt. The attack was particularly severe at the melt-gas interface when tests were made with partially submerged specimens of the metals.

Further studies were made on the permeation of a six-inch graphite crucible by molten sodium fluoride-zirconium fluoride. Analytical data obtained from sections of the crucible indicated that about one-third of the voids in the graphite were filled after 144 hours exposure to the fused salt under 1000 mm pressure. Uranium (as the tetrafluoride) was added to the melt after 24 hours exposure of the crucible to the melt alone. Analyses of the crucible showed a decreasing uranium concentration toward the outside of the crucible wall. Both the fused salt concentration in the graphite and the uranium concentration in the salt increased with longer exposure times.

Carrier-free tracer experiments were performed on the behavior of niobium and ruthenium in the fused fluoride process. Niobium was removed effectively from a hydrogen fluoride stream by a sodium fluoride trap. Earlier results which indicated that ruthenium is not volatilized from molten sodium fluoride-zirconium fluoride by fluorine sparging were confirmed with tracer ruthenium.

Work on the study of plutonium fluorides during the quarter has been confined to the construction and testing of new laboratory apparatus.

Pilot plant operations were directed toward development of two operations basic to fluoride volatility processes, namely, the fused fluoride dissolution of uranium-zirconium alloy fuels and the purification of uranium hexafluoride by fractional distillation.

During the quarter discussions were held with representatives of Horizons, Inc., Cleveland, Ohio and G. W. Watson and C. J. Barton of ORNL relative to fluoride volatility processing.
A. Laboratory Investigations  
(R. K. Steunenberg)  

1. Fused Salt Processing of Enriched Reactor Fuels  
   a. Corrosion  
      (W. B. Sedfeldt, L. Hays, R. Breyne)  

   Testing of potential materials of construction for use with the fused fluoride volatility processing of zirconium matrix fuels continued. Additional coupon tests in fluorinated melts were made. Experiments in hydrofluorinated melt environments directed toward the processing of the LMFR core fluid are found elsewhere in this report (see LMFR section, page 30). The results from these experiments are in greater part applicable to STR fuel processing as well.  

   All tests reported here, unless otherwise indicated, were made in fluorinated equimolar sodium fluoride-zirconium fluoride melts at 600 C.  

   Two types of tests were made: (1) coupon tests in which metals were exposed to the sparged melt phase, and (2) simulated draft tube test in which strips of metal were wired together to form a rectangular cross section, and partially immersed in the melt; fluorine was then introduced centrally below the melt level. The results are reported in Table 1. All of the materials tested, except gold, appear to have limited usefulness if fully submerged in fluorine sparged melt. However, simultaneous exposure to vapor phase, interface, and sparged liquid phase causes rapid attack at the interface with all metals tested, except Hastelloy B. These would not be acceptable for a fluorination vessel.  

   The Hastelloy B test was the longest of those made: fluorine sparge for 21 hours plus helium sparge for 34 hours. The rates of attack indicated in Table 1 are based on fluorine exposure time only. A hard dark film, varying in thickness from 0.2 to 2.3 mils, was found on the single strip that was sectioned. It is not known whether this film is protective. Dimensional changes were obtained by microscopically measuring sound metal remaining. These changes were a maximum of 3.2 mils at the interface, compared to a typical 0.4 mil in the liquid phase, and up to 1.8 mils in the vapor phase. Some intergranular attack (up to 1.4 mils) occurred in the vapor phase near the tip of the strip; none was observed at the interface or in the liquid phase.  

   b. Graphite Permeability Studies  
      (S. Vogler, J. Fischer, G. Redding)  

      A graphite dissolver is to be used in pilot-plant investigations of the fused fluoride process for zirconium-enriched uranium fuel
Table 1

DIMENSIONAL CHANGES OF VARIOUS METALS IN FLUORINATED FUSED SALTS

<table>
<thead>
<tr>
<th>Salt:</th>
<th>Equimolar NaF-ZrF₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt Weight:</td>
<td>300 g</td>
</tr>
<tr>
<td>Liner:</td>
<td><em>A</em> Nickel, 1½ in. OD, 0.032 in. wall</td>
</tr>
<tr>
<td>Sparge Tube:</td>
<td><em>A</em> Nickel, 1/4 in. OD</td>
</tr>
<tr>
<td>Test Component, Submerged Tests:</td>
<td>Coupon</td>
</tr>
<tr>
<td>Test Component, Partially Submerged Tests:</td>
<td>Draft tube fabricated from four metal strips, 6 in. x 0.5 in. x 0.032 in.</td>
</tr>
<tr>
<td>Temperature:</td>
<td>600 C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run</th>
<th>Material</th>
<th>Exposure Type and Time, (\text{hr})</th>
<th>(F_2) rate, g/hr</th>
<th>Dimensional Change, Maximum Measured, mils/mils/mo</th>
<th>Calculated From Weight Loss, mils/mils/mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>Gold</td>
<td>S 7</td>
<td>11.5</td>
<td>0.4</td>
<td>410</td>
</tr>
<tr>
<td>118</td>
<td>Platinum</td>
<td>S 7</td>
<td>11.5</td>
<td>0.5</td>
<td>51</td>
</tr>
<tr>
<td>120</td>
<td>Copper</td>
<td>S 7</td>
<td>10.7</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>121</td>
<td>Copper</td>
<td>S 7</td>
<td>10.7</td>
<td>0.5</td>
<td>51</td>
</tr>
<tr>
<td>120</td>
<td>Tungsten</td>
<td>S 7</td>
<td>12.3</td>
<td>0.07</td>
<td>7</td>
</tr>
<tr>
<td>121</td>
<td>Tungsten</td>
<td>S 7</td>
<td>12.3</td>
<td>0.5</td>
<td>51</td>
</tr>
<tr>
<td>122</td>
<td>Silicon Carbide</td>
<td>S 7</td>
<td>8.5</td>
<td>0.5-2</td>
<td></td>
</tr>
<tr>
<td>126</td>
<td>Molybdenum</td>
<td>D 0.8</td>
<td>11</td>
<td>11</td>
<td>1000</td>
</tr>
<tr>
<td>127</td>
<td>Silver</td>
<td>D 4</td>
<td>10.3</td>
<td>12</td>
<td>1000</td>
</tr>
<tr>
<td>130</td>
<td>Gold</td>
<td>D 1.3</td>
<td>11.4</td>
<td>11</td>
<td>1000</td>
</tr>
<tr>
<td>131</td>
<td>Copper</td>
<td>D 6.5</td>
<td>13.4</td>
<td>32</td>
<td>1000</td>
</tr>
<tr>
<td>132</td>
<td>Platinum</td>
<td>D 5</td>
<td>11.2</td>
<td>14</td>
<td>1000</td>
</tr>
<tr>
<td>133</td>
<td>Silicon Carbide</td>
<td>D 1.7</td>
<td>11</td>
<td>110</td>
<td>0.7</td>
</tr>
<tr>
<td>135</td>
<td>Hastelloy B</td>
<td>D 21</td>
<td>13.9</td>
<td>3.2</td>
<td>110</td>
</tr>
</tbody>
</table>

\(a\)S = sample submerged; exposed to sparged melt
\(D\) = partially submerged; exposed to sparged melt, interface, and vapor phase
\(b\)Two methods: micrometer and microscope; in all cases, maximum attack was observed at interface.
\(c\)Useful only if attack is uniform
\(d\)Portion of "Globar" heating element
\(e\)Twenty-one hours of fluorine sparge plus 34 hours of helium sparge

Alloys. Among the factors to be considered in the use of graphite is its permeability to the sodium fluoride-zirconium fluoride-uranium tetrafluoride fused salt. Previously reported experiments on a smaller scale had shown that there is little, if any, dimensional change in a graphite system when hydrogen fluoride is passed through a sodium fluoride-zirconium fluoride melt at 600 C. Some of the molten salt, however, passed into the graphite wall. In certain instances the wall was penetrated completely by the salt.

In the previous quarterly report (ANL-5820, page 22) a unit in which permeability tests could be conducted was described. The apparatus
was constructed in such a way that gas pressure could be applied to the melt to simulate the hydrostatic pressure which would develop in a large dissolver.

In a preliminary experiment (Run 3), 2100 grams of equimolar sodium fluoride-zirconium fluoride was used, giving a melt depth of 5 1/2 inches. This melt was kept at 625 C for 70 hours, at which time 9.3 grams of uranium tetrafluoride was added. After another 50 hours at temperature, the experiment was terminated by removing the heater. After cooling, the crucible containing the solidified salt was removed and sectioned with a hacksaw. Microscopic examination of a polished portion of the sectioned crucible revealed that the melt had penetrated about 1/4 inch into the 1 1/2-inch crucible wall.

In Run 4, a 2250-gram charge of sodium fluoride-zirconium fluoride was placed in the crucible and the temperature was raised to approximately 630 C. The melt was held in the crucible under 1000 mm helium pressure for 24 hours; then an eight-gram charge of uranium tetrafluoride was added to the melt. The uranium-containing melt was allowed to solidify. Upon removing the crucible from the apparatus, it was discovered that the upper portion of the graphite crucible was cracked in several places. The cracking was believed to result from differences in thermal expansion of the steel sleeve inside the crucible and the graphite. Salt had penetrated through the bottom of the crucible, probably through connected voids parallel to the axis of extrusion of the graphite. A section of the crucible from the midportion of the hot zone was polished and examined microscopically. It was found that the salt had penetrated the crucible to within 1/16 inch of the outer wall.

The crucible was sectioned by taking pie-shaped parallel slices perpendicular to the main axis of the crucible. One of these slices from the mid-section of the heated zone was used to prepare samples for analysis, as indicated in the following sketch.

The samples were obtained by taking drillings from these positions. The diameter of each hole was 6.0 mm and its depth was 38.4 mm. The centers of the holes were the following distances (in mm) from the inside wall:

| 1, 6 | 5.2 | 4, 24.6 |
| 2   | 10.6| 5, 8, 32.8 |
| 3, 7 | 16.9|          |
The drillings from each of the samples were analyzed for uranium and total ash. Preliminary experiments permitted an empirical correlation between the percentage ash found and the salt content. For example, type CS graphite has an ash residue of 0.19 per cent, and this value is first subtracted from the determined ash analysis. A further empirical correction was established by ashing samples of graphite and salt in the appropriate ratios. The data from Run 4, corrected by this method, are summarized in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Penetration of Type CS Graphite by Molten Sodium Fluoride - Zirconium Fluoride Under Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of Melt: 22.0 g</td>
</tr>
<tr>
<td>Weight of UF₄ Added: 5 g</td>
</tr>
<tr>
<td>Helium Pressure: 1000 mm</td>
</tr>
<tr>
<td>Pretreatment of Crucible: Melt held at 630°C under 1000 mm helium for 24 hr</td>
</tr>
<tr>
<td>Temperature: 630°C</td>
</tr>
<tr>
<td>Sample No.</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>Run No.</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

Based on the apparent and true densities of graphite; the maximum salt concentration, if all the voids were filled, would be 32.5 weight per cent.

Salt determinations were made only on Samples 1, 3, and 5.

Run 5 was essentially a repetition of Run 4, except the melt was held in the crucible for a longer period. The melt, pressurized with 1000 mm of helium, was kept in the graphite crucible for 24 hours, after which 7.5 grams of uranium tetrafluoride were added to the system. The melt was then held under 1000 mm helium pressure for an additional 120 hours.

When the cover was removed from the apparatus, it was found that the melt level had fallen below the steel pipe insert. This resulted from permeation of the fused salt through the bottom of the crucible. In this experiment the crucible was sectioned in a slightly different manner. A 1/2-inch slice perpendicular to the axis of the crucible was taken 1/4-inch from the bottom. A pie-shaped section was cut from this slice, and this section was cut as shown. Each of the samples was submitted for uranium and total ash analyses.
The results show a decrease in salt concentration with distance from the inside wall of the crucible. There is also a decrease in the uranium content of the salt. A comparison of the data from Runs 4 and 5 in Table 2 shows that longer exposure times of the melt under pressure result in higher salt concentrations in the graphite and higher uranium concentrations in this salt. Using the apparent and true densities of graphite, it is possible to calculate that the salt concentration in the graphite would be 32.5 weight per cent if all the voids were occupied. The data in Table 2 indicate that after 144 hours under pressure the molten salt had filled approximately one-third of the voids.

c. **Fission Product Studies: Carrier-free Tracer Investigations with Niobium and Ruthenium**

(L. E. Trevorrow, J. Fischer, H. D. Tyler, W. A. Shinn)

Experiments were reported previously on the behavior of niobium and ruthenium fluorides in fused sodium fluoride-zirconium fluoride (ANL-5820, page 23). Unlike these studies, which involved gram quantities of niobium and ruthenium, the following work involved carrier-free tracer. The isotopes used were niobium-95 and ruthenium-rhodium-106. The purpose of this work was to simulate to a certain extent the behavior of fission product niobium and ruthenium in a fused fluoride process.

Niobium. It has been shown previously that niobium is volatilized to a large extent by hydrofluorination of the fused salt (ANL-5820, page 25). One of the methods proposed for the removal of volatilized niobium from uranium hexafluoride consists of absorbing it on solid sodium fluoride beds. It was therefore of interest to determine whether a similar procedure could be used to remove fission product niobium from a recycled hydrogen fluoride stream. It is shown that hydrogen fluoride is absorbed by sodium fluoride, forming a complex compound. The relative stabilities of this complex and the one formed between sodium fluoride and niobium pentafluoride are not known. The gram-scale experiments with unirradiated niobium metal suggested that the niobium pentafluoride is absorbed in preference to hydrogen fluoride. The purpose of the following experiments was to compare the behavior of carrier-free niobium tracer. In such an experiment the ratio of hydrogen fluoride to niobium is extremely large.

The niobium-95 was obtained from the Oak Ridge Radioactive Isotopes Division as an oxalate solution. The identity of the material was verified by a gamma-ray analyzer.

The apparatus consisted essentially of a 3/8-inch nickel line bent to form three U-traps in series. The middle trap contained a six-inch section packed with sodium fluoride powder. The third trap was a cold trap cooled by dry ice. The sodium fluoride was dried in place by heating under vacuum; then the entire apparatus was prefluorinated for several hours at 100 to 150 C with bromine pentafluoride vapor.

The first step of the experiment was to evaporate an aliquot of the niobium-95 oxalate solution on a nickel disk. Approximately $2 \times 10^{-4}$ millicurie of niobium-95 was used. The disk was then placed in molten sodium fluoride-zirconium fluoride which was sparged with fluorine. The resulting niobium-95 fluoride was transferred by volatilization in the fluorine stream into the first U-trap (at dry ice temperature) where it was condensed. Hydrogen fluoride was passed through the trap system. The temperature of the system was maintained at 250 to 275°C, and the gas flow was continued for about five hours. During this time 12 g of hydrogen fluoride passed through the system.

At the end of the experiment the nickel line was monitored with a portable scintillation counter. The hard gamma radiation of niobium-95 (0.75 Mev) was detected easily through the nickel tubing. The scintillation crystal was enclosed in a lead probe which served to collimate the beam normal to the tubing. The lead shield was also equipped with guides which served to maintain a constant counting geometry as the probe was moved along the tubing. This method of counting does not give a strictly quantitative result, but the data are useful for comparative purposes.

The results of an experiment are shown in Figure 1. Most of the niobium activity was trapped by the sodium fluoride, whereas the entire 12 grams of hydrogen fluoride passed through the system. The small peak evident in the first trap indicates that not all the niobium was volatilized. When it is realized that only about $10^{-12}$ gram of niobium was used in the experiment, it is not surprising that quantitative transfers were not achieved.

Ruthenium. Previous work (ANL-5820, page 24) had indicated that ruthenium is not volatilized from fused sodium fluoride-zirconium fluoride by sparging with fluorine or hydrogen fluoride. In order to compare these results from gram quantities of unirradiated ruthenium with the behavior of carrier-free tracer, the following experiment was performed.

Ruthenium-106-rhodium-106 carrier-free tracer was obtained from Oak Ridge as a complex chloride solution. Approximately $5 \times 10^{-2}$ mc of the tracer was reduced to the metal with magnesium and
carried on 10 mg of freshly precipitated palladium metal. The palladium precipitate was filtered and dried over Drierite for about 24 hours. The metal was then added to an equimolar sodium fluoride-zirconium fluoride melt which had been pretreated for three hours with fluorine. The nickel off-gas line, which was maintained at 300 C, terminated in a U-trap kept at 30 C.

The melt, containing the tracer at 600 C, was sparged with fluorine for three hours. At the end of the experiment the off-gas line was monitored with the same equipment used in the niobium experiments.

The counting rates of the off-gas lines were essentially at background level. It was found that 5 x 10^{-4} mc (one per cent of the activity used in the sparging experiment) placed in nickel tubing similar to the off-gas line gave a counting rate approximately twice the background level. Since one or two per cent of the activity would have been detected if it had volatilized, it was concluded that less than one per cent of the ruthenium added to the melt was volatilized by the fluorine sparge.

2. Plutonium Fluoride Studies
(M. J. Steindler, L. E. Trevorrow, D. V. Steidl, W. A. Shinn)

Work during the quarter has consisted primarily of construction of new laboratory apparatus. One unit which has been completed is designed to investigate the fluorination rates of uranium and plutonium fluorides and oxides. The other, which is nearing completion, is aimed toward a study of the handling and decomposition reactions of plutonium hexafluoride.

B. Pilot Plant Operations
(W. J. Mecham)

1. Fused-Salt Pilot Plant
(R. W. Kessle, J. Gabor, W. Pehl)

In the fused fluoride volatility process for the recovery of enriched uranium from zirconium-alloy reactor fuels, two high-temperature steps are involved. The fuel alloy is dissolved by hydrofluorination in a molten sodium fluoride-zirconium fluoride mixture, and the uranium hexafluoride is then volatilized from the fused salt by sparging with fluorine or an equivalent fluorinating agent. A graphite dissolver-hydrofluorinator for this process has been undergoing design and operational tests at Horizons, Inc. A description of the equipment and a discussion of the operational tests are given in the following two sections.

Equipment

The test assembly consisted of two graphite vessels (a salt premelt vessel and the dissolver), together with facilities for providing hydrogen
fluoride sparge gas and for handling dissolver off-gas. A schematic flow diagram is shown in Figure 2. The flow streams in this figure show the charging of solid salt to the pre-melt vessel and the transfer of molten salt to the dissolver. The fuel elements were charged directly to the dissolver through an air lock. Argon was used as a purge gas. The hydrogen fluoride was stored as a liquid and vaporized from a weigh tank to provide the dissolver sparge gas. The dissolver off-gas was put through two dust traps and a dry ice-cooled condenser to recover the bulk of unreacted hydrogen fluoride. The hydrogen fluoride vessels were manifolded so that they could be used interchangeably as boilers and condensate receivers. In the test unit limestone towers were used in the vent system to remove hydrogen fluoride vapor.

The graphite, high-temperature vessels were provided with internal electric resistance heaters so that the external wall could be kept relatively cool. A sectional diagram of the dissolver is given in Figure 3, showing internal structure (except for the heaters). As seen in the figure, lampblack thermal insulation is packed between the internal graphite wall and the external shell. It is in this insulation zone that the wall temperature gradient falls below the salt melting point. The advantage of this design is that the cold wall prevents any salt leakage from the system, even if the graphite has some permeability to the molten salt. Vapor sealing is achieved by the water-cooled flange on the metal shell.

A diagram of heater construction is given in Figure 4. Most of the heat was generated in the smaller cross-section central graphite rod. The outer graphite shell served as a current return and as a structural...
support for the replaceable heater unit. Argon purge gas was introduced at the top of the heater into the annulus between the central heating rod and the shell. A hole near the bottom of the shell served as purge gas exit. The object of the purge was to provide maximum protection of the heater rod from oxidation. Two such heaters were provided for each graphite vessel. The temperature control for each vessel was achieved by a 30-kW saturable-reactor power supply.

**Operational Tests**

At Horizons preliminary operational tests were successfully carried out on the basic steps of salt melting and transfer, and dissolution of simulated zirconium alloy fuel elements.

The only corrosive attack on graphite components during these tests under processing conditions was suffered by the heating elements.
Most of this attack was due to the presence of oxygen; such corrosion should be decreased by suitable operating procedures. In the case of the pre-melt vessel, however, there also appeared to be severe attack of the heater rods by molten sodium fluoride.

There are two differences between conditions in the pre-melt vessel and the dissolver which influence heater attack. (1) Initial salt fusion takes place in the pre-melt vessel; in this step some residual moisture is released, which can attack the heater rods. (The salt is transferred to the dissolver in the molten state.) (2) Pure sodium fluoride is fused in the pre-melt vessel as make-up charge to the dissolver, where dissolution of zirconium metal forms the approximately equimolar mixture of sodium fluoride and zirconium fluoride. The dissolver thus operates with the lower-melting mixture at about 600°C, while the pre-melt vessel is operated at 1200°C in order to be safely above the melting point of pure sodium fluoride (about 1050°C). Thus conditions are more severe in the pre-melt vessel.

Although more severe attack on the pre-melt heaters was encountered, heaters can be more readily replaced, since this operation involves no radioactivity.

Program

Installation has begun of the all-graphite dissolver-hydrofluorinator developed by Horizons, Inc. for component evaluation and fuel element dissolution studies. Facilities will include a full-size fuel element charger, a hydrogen fluoride sparge system and an off-gas handling system. The installation is planned for completion at the end of the next quarter.

2. Distillations Studies

The use of fractional distillation as a means of producing very pure uranium hexafluoride is a key step in various fluoride volatility processes.

a. Pilot Plant Column
   (R. W. Kessie, M. Deerwester, A. Freeman)

Preparations are being made for tests of the two-inch packed pilot plant distillation column in the production of very pure uranium hexafluoride product from a binary containing bromine pentafluoride.

b. Vapor-Liquid Equilibria
   (R. C. Liimatainen, A. Freeman)

Vapor-liquid equilibria of the system uranium hexafluoride-bromine pentafluoride are to be investigated in equipment recently constructed. Preliminary runs have been made.
c. Laboratory Fractionating Column Studies
(F. Mertes, R. C. Liimatainen)

A laboratory-scale fractionating column* was put into operation to assist in the investigation of volatility separations studies involving uranium hexafluoride. A schematic diagram of the equipment is given in Figure 5.

**FIGURE 5**
LABORATORY FRACTIONATING COLUMN

Equipment and Procedure

The column has a 94-inch section, 1/2-inch in diameter, packed with 1/8-inch single-turn nickel helices. All components in contact with the process fluid are of nickel, except for a Fluorothene sight glass on the take-off line. Booth-Cromer null-balance-type pressure transmitters were used to measure column pressure drop. Provision was made for addition of fluorine and removal of samples.

Still pot and lines were electrically heated, and the entire column was insulated and enclosed in a ventilated hood. The temperature of the condenser cooling water was adjusted by a constant-temperature circulating system to avoid sub-cooling of condensate.

The column was prefluorinated with bromine pentafluoride and fluorine. Charging was accomplished by vaporizing material into the still pot and column system.

*Initial design and installation were done by J. Fischer and G. Redding.
Pressure Drop Measurements

A series of tests were made to determine the pressure drop across the column during distillation of bromine pentafluoride and uranium hexafluoride at various boil-up rates. The results obtained with each of these pure components, given in Figure 6, showed that the uranium hexafluoride flooding point and the break point in the bromine pentafluoride curve occurred at a boil-up of about 0.23 g-mol/min. The bromine pentafluoride flooding point was about 0.34 g-mol/min. The corresponding superficial linear vapor velocities at flooding were 1.39 and 1.88 ft/sec, respectively, for uranium hexafluoride and bromine pentafluoride.

**FIGURE 6**
DISTILLATION OF BROMINE PENTAFLUORIDE AND URANIUM HEXAFLUORIDE; EFFECT OF BOIL-UP RATE ON PRESSURE DROP
Preliminary HETP Determination

A mixture of uranium hexafluoride and bromine pentafluoride was charged to the column to determine HETP. The column was allowed to run overnight at total reflux; then samples of overhead and still pot vapor were taken and analyzed for uranium. The results are given in Table 3. The number of plates was calculated by the Fenske equation, assuming ideal Raoult's Law behavior. The values of HETP obtained (8 to 12 inches) are somewhat higher than expected, and a further check will be made.

Table 3
HETP FOR DISTILLATION OF URANIUM HEXAFLUORIDE - BROMINE PENTAFLUORIDE BINARY MIXTURE
1/2-inch ID Packed Column

<table>
<thead>
<tr>
<th>UF₆ in Still Pot Vapor (mol %)</th>
<th>UF₆ in Overhead (mol %)</th>
<th>Superficial Vapor</th>
<th>Total Pressure (psia)</th>
<th>Number of Plates</th>
<th>HETP (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.6</td>
<td>5.38</td>
<td>0.169</td>
<td>0.57</td>
<td>55</td>
<td>8.1</td>
</tr>
<tr>
<td>66.2</td>
<td>1.7</td>
<td>0.173</td>
<td>0.65</td>
<td>49</td>
<td>12.7</td>
</tr>
</tbody>
</table>

Program

The first use of this column will be to fractionate uranium hexafluoride made by the fluorination of crude uranium tetrafluoride derived from acid-leached uranium ore concentrate.
II. LIQUID METAL FUEL REPROCESSING
(J. Fischer)

A major portion of the laboratory investigation within the group has been directed towards the development of a fluoride volatility process to recover and purify the core fluid from the Liquid Metal Fuel Reactor (LMFR). Uranium-233 dissolved in bismuth (maximum uranium concentration about 1350 ppm) is the fuel. The proposed fluoride volatility flowsheet involves fused salt extraction of core fluid with a hydrogen fluoride sparge. This removes uranium, as the tetrafluoride, plus the majority of the fission products, as fluorides. The uranium tetrafluoride is converted to uranium hexafluoride and the uranium hexafluoride purified by distillation. The uranium is then reduced to the metal, returned to the bismuth and thence to the reactor. Most of the laboratory work of the past quarter has consisted of assembling and testing new equipment.

Corrosion tests of materials of construction having potential use in the fluoride volatility process for reprocessing LMFR core fluid showed silver, gold, molybdenum and platinum to have promise when in contact with hydrofluorinated sodium fluoride-zirconium fluoride melts. The corrosion effects of the contact of bismuth and fused sodium fluoride-zirconium fluoride on molybdenum are being studied. Molybdenum appears to be very resistant to attack in this medium.

Conferences regarding LMFR processing were held with representatives of Babcock and Wilcox.

A. Laboratory Investigations


The objectives of the laboratory and a general description of the equipment to be used were given in the last quarterly report, ANL-5820, pages 34 to 45.

Much of the work in the past quarter has been spent in assembling and testing new equipment.

Apparatus for the equilibrium studies of the extraction of fission products from liquid bismuth with sodium fluoride-zirconium fluoride fused mixtures is being built. Tests are in progress to determine the chemical reactivity of fluorine with molten bismuth. Methods of preparing bismuth alloys are being studied. Alloy-preparation furnaces have been built and preliminary work on the preparation of uranium-bismuth ingots is in

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*Special Scientific Employee on loan from Union Carbide Nuclear Co.
progress. Equipment is being set up for studying the removal of noble fission products from bismuth. Equilibrations of bismuth, zinc and ruthenium will be made to obtain a distribution coefficient for ruthenium. Some similar work is being done by American Smelting and Refining.

An analytical procedure for the determination of uranium in bismuth, which utilizes a separation of the uranium from the bismuth, has been developed. The separation is accomplished by amalgamating the bismuth and dissolving the uranium in a solution of 4 M HCl and 0.5 M HF. Uranium is then analyzed polarographically in a sodium acetate-EDTA solution. The detailed analytical procedure for the determination of uranium in bismuth is described in Section VI, page 127.

B. Corrosion Studies
(W. Seefeldt, R. Breyne, L. Hays)

A program has been started to determine what materials of construction may offer a potential for satisfactory use in the presently envisioned volatility processing scheme for the LMFR core fluid. In general the requirements for such a material are compatibility with bismuth, sodium fluoride-zirconium fluoride, and anhydrous hydrogen fluoride at temperatures in the vicinity of 600 °C.

Initial exposures of test materials were to the salt and hydrogen fluoride in the liquid phase only (see ANL-5820, pages 45 to 48). Tantalum and niobium dissolved readily, but silver, gold, platinum, and molybdenum appeared promising. Further tests were made with the latter materials during the quarter. Croloy 24 was tested in hydrofluorinated bismuth.

Method

Promising materials were exposed in a partially immersed condition. A simulated draft tube was made by wiring four strips of the metal together to form a rectangular cross section. The strips were six inches long and one-half inch wide. This assembly was partially immersed in equimolar sodium fluoride-zirconium fluoride, and anhydrous hydrogen fluoride was introduced centrally below the melt to provide alternate liquid-gas contacting of the internal surfaces.

Following exposure the strips were cleaned by immersion in a molten chloride bath at 600 °C. The strips were then evaluated for both dimensional and metallurgical changes, the former by weight loss and direct measurement (micrometer and microscope), the latter by metallographic techniques. Silver and molybdenum were exposed for longer periods, the former because of its relatively lower cost, the latter because of its known superior resistance to molten bismuth.
**Results**

The dimensional changes are shown in Table 4. All of the materials tested showed very low rates of attack, and none showed any appreciable loss in ductility.

**Table 4**

**DIMENSIONAL CHANGES OF VARIOUS METALS IN HYDROFLUORINATED FUSED FLUORIDE MELTS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Exposure Time (hr)</th>
<th>HF Rate (g/hr)</th>
<th>Maximum Measured</th>
<th>Calculated from Weight Loss&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>72</td>
<td>23.7</td>
<td>0.2 &lt; 2</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>72</td>
<td>25.7</td>
<td>&lt; 1 &lt; 10</td>
<td>0.008</td>
</tr>
<tr>
<td>Gold</td>
<td>72</td>
<td>22.6</td>
<td>&lt; 1 &lt; 10</td>
<td>0.02</td>
</tr>
<tr>
<td>Silver</td>
<td>647</td>
<td>27.2</td>
<td>0.3 0.32</td>
<td>0.02 0.03</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>445</td>
<td>21</td>
<td>0.1 0.16</td>
<td>0.07 0.1</td>
</tr>
<tr>
<td>Platinum</td>
<td>72</td>
<td>26.0</td>
<td>0.2 2</td>
<td>0.3 3</td>
</tr>
</tbody>
</table>

<sup>a</sup> Figure valid only if corrosion is uniform.

The platinum specimen was attacked in an intergranular manner at the interface and at the lower end exposed to the liquid phase. The remaining portions of the metal were free from such attack.

Tiny blisters formed on the surfaces of the silver strips, and metallography revealed the formation of subsurface voids. In the portion of the simulated draft tube that had been immersed, void formation was greater on the inside (exposed to sparged melt) than on the outside (exposed to non-sparged melts), 7.5 mils compared to 5.9 mils. In the vapor phase, this difference did not exist, being 7.0 mils on both sides. The formation of these voids is probably due to the high oxygen content of the silver. Corrosion-product hydrogen diffuses into the metal, reacts with oxide impurities to form steam, and the expanding steam forms the voids. An oxygen-free form of silver would be needed for this service.
Croloy 2\(\frac{1}{4}\) is known to have resistance to molten bismuth. In a single test, a piece of 1/4-inch schedule 80 pipe made of Croloy 2\(\frac{1}{4}\) was used as a sparge tube to introduce hydrogen fluoride into molten bismuth at 600 C. Exposure was for a total of 72 hours at a gas rate of 11.8 grams per hour. The portion of the Croloy 2\(\frac{1}{4}\) that was immersed in the bismuth was not attacked; the vapor phase showed severe corrosion, with the formation of thick voluminous layers of iron fluoride.

A test was recently started in which molybdenum was exposed to bismuth, sodium fluoride-zirconium fluoride, and hydrogen fluoride simultaneously. Visual examination after 200 hours indicated little attack.
III. **FLUIDIZATION STUDIES**  
(A. A. Jonke)

Development work continued on the fluid-bed drying of zirconium-uranium-fluoride solutions. Efforts were concentrated on the spraying of solutions containing precipitated uranium tetrafluoride. This is an intermediate step in the proposed fluorination process for separation of uranium from high zirconium-low uranium alloys. Difficulties, such as nozzle caking and particle growth in the bed, continued over a wide range of variables. Some success in operations has been achieved at temperatures near 300 C.

Laboratory studies were made to evaluate reducing agents which will completely and quickly precipitate the uranium tetrafluoride in the feed solutions to the fluid-bed driers. Other tests are being conducted to find additives for the zirconium-uranium solutions which will increase the porosity of the solids produced and permit complete separation of the uranium during fluorination.

Work on fluid-bed calcination of waste solutions has been directed toward equipment modifications, the determination of non-volatile fission product activity in the gas, the utility of carbon monoxide in reducing ruthenium volatilization and providing internal heat generation, ignition testing of the solid product at elevated temperatures to study fission product volatilization behavior, and a bench-scale test of a new proposal for filter blowback.

Application of a fluid-bed technique to apply a ceramic-glaze coating on calcined oxide continued. Some study has been made of the feasibility of improving the heat transfer characteristics of the oxide by compacting with powdered metal.

Qualitative mixing studies have started in straight and tapered fluidized bed columns. Mixing coefficients will be measured using a radioactive pulse-tracer technique. A mathematical analysis of the problem is presented.

A pilot-plant study of the fluidized-bed fluorination of uranium tetrafluoride to uranium hexafluoride is under way. Fluidized-bed fluorination offers a means of producing uranium hexafluoride from various granular uranium-bearing materials, with advantages attendant to non-aqueous, fluidized solid-gas systems. Tests made on refined green salt showed temperature had a large effect on fluorine efficiency (maximum efficiency 91 per cent at 450 C), while fluorine concentration had a small effect. Fluorine concentrations above 43 per cent could not be controlled due to limitations on heat removal.
The following discussions and conferences were held during the quarter:

(1) Feed materials conferences held by United States and United Kingdom representatives at National Lead, Fernald, Ohio, and at the Weldon Springs Plant of Mallinckrodt Chemical Co., St. Louis, Mo., were attended March 25th through March 28th.

(2) A two-day meeting on feed materials processing and fluidization technology held March 31st and April 1st at ANL was attended by representatives of the United Kingdom, National Lead, K-25 (ORNL), Mallinckrodt, and ANL.

(3) With representatives of Phillips Petroleum Co. concerning waste calcination.

(4) With Brookhaven National Laboratory personnel on waste calcination.

(5) With Hanford Atomic Power Operations representatives in regard to waste calcination.

A. Separation of Uranium from Zirconium-Uranium Fuel Alloy

Work has continued on developing a process whereby uranium can be quantitatively recovered from zirconium-uranium alloy fuel elements. The process, in the present stage of development, starts with the dissolution of the alloy in aqueous hydrofluoric acid to give a fluoride/zirconium ratio of 4.5 and a zirconium concentration of 1.5 M. This solution is evaporated and calcined in a fluidized-bed reactor. The uranium is recovered from the calcined solids as the volatile hexafluoride during a subsequent reaction with fluorine gas.

1. Fluidized-Bed Drying
   (N. Levitz, A. Litty, J. Barghusen, O. Sandus, D. Finley, M. Jones, D. Raue)

   During this period efforts continued to determine operating conditions which would permit continuous fluid-bed drying of hydrofluoric acid solutions of zirconium and uranium. Some difficulties were reported last quarter (ANL-5820, page 56) in runs at a nozzle atomizing pressure of 30 psig; so a series of runs were made in the three-inch diameter Monel column at a lower pressure, 15 psig. The feed solution for these runs was a simulated STR-type, 1.5 M zirconium, 0.007 M uranium and fluoride-to-zirconium ratio of 4.5. The column conditions were 350 C bed temperature.

*Special Scientific Employee on loan from General Chemical Division of Allied Chemical and Dye Corporation.
2 ft/sec fluidizing gas velocity, and 17 ml/min feed rate. Total running time was 18.3 hours (about 6 hours running time on each of three successive days) with no operating difficulties and essentially no growth in bed particle size. Sieve analyses of product samples are summarized in Table 5. The minus 200 fraction decreased from 11 per cent to 4.2 per cent while the plus 20 fraction increased slightly from 3.8 to 7.2 per cent. There was an increase in tapped bulk density from 1.7 to 2.0 g/cu cm.

Table 5

SUMMARY OF SCREEN ANALYSES OF SOLIDS FROM FLUID-BED DRYING
OF ZIRCONIUM FLUORIDE-HYDROFLUORIC ACID SOLUTION

Runs ZC-63 through ZC-65

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run Time (hr)</th>
<th>Bulk Density (g/cc)</th>
<th>Percentage in Indicated Size Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Untapped Tapped</td>
<td>+20 +40 +60 +100 +200 +325 +6325</td>
</tr>
<tr>
<td>Starting Bed</td>
<td>0</td>
<td>1.6 1.7</td>
<td>3.8 38 35 12 6.1 2.2 2.7</td>
</tr>
<tr>
<td>Product No. 1</td>
<td>0.7</td>
<td>1.8 1.9</td>
<td>5.7 42 28 14 7.7 0.8 0.8</td>
</tr>
<tr>
<td>Product No. 2</td>
<td>2.7</td>
<td>1.8 2.0</td>
<td>5.3 36 27 21 8.0 0.7 1.3</td>
</tr>
<tr>
<td>Product No. 3</td>
<td>5.8</td>
<td>1.8 2.0</td>
<td>7.6 38 26 21 4.4 1.0 1.2</td>
</tr>
<tr>
<td>Product No. 4</td>
<td>7.1</td>
<td>1.8 2.0</td>
<td>8.4 41 25 21 2.6 1.0 0.8</td>
</tr>
<tr>
<td>Product No. 5</td>
<td>8.3</td>
<td>1.9 2.0</td>
<td>5.5 34 27 29 1.8 0.7 1.3</td>
</tr>
<tr>
<td>Product No. 6</td>
<td>12.2</td>
<td>1.6 2.0</td>
<td>7.4 37 36 16 1.6 1.0 0.8</td>
</tr>
<tr>
<td>Product No. 7</td>
<td>13.3</td>
<td>1.9 2.0</td>
<td>7.2 36 46 7.6 1.0 1.1 0.5</td>
</tr>
<tr>
<td>Final Bed</td>
<td>18.3</td>
<td>1.8 2.0</td>
<td>7.2 33 48 8.2 1.4 1.8 1.0</td>
</tr>
</tbody>
</table>

Work performed during the previous quarter (ANL-5820 page 59) showed that the uranium recovery from the zirconyl fluoride-uranium tetrafluoride matrix formed during fluid-bed drying operations can be materially increased if the uranium is present as discrete particles of uranium tetrafluoride. The tetrafluoride is readily precipitated from the zirconium-uranium feed solution by increasing the fluoride/zirconium ratio from 4.5 to 10 by the addition of hydrofluoric acid. Work during this quarter was directed primarily toward the study of the fluid-bed drying of these slurries of uranium tetrafluoride. Laboratory studies showed that the precipitate initially forms as a colloid which gradually transforms to a crystalline state. When the transformation has progressed sufficiently, discrete particles begin to settle from the solution. The
transformation from the colloidal state to the crystalline state usually commences in about one to three minutes in dilute (0.007 M) uranium solution. In more concentrated uranium solutions (0.03 M) the transformation is extremely rapid: particles begin to settle from solution immediately after hydrofluoric acid is added.

For the dissolution of zirconium-uranium alloys containing over 2 per cent uranium, the addition of an oxidizing agent to the hydrofluoric acid is necessary in order to dissolve the uranium completely. Laboratory studies have shown that chromium trioxide is a satisfactory oxidant. The precipitation of uranium tetrafluoride from such solutions prior to fluid-bed drying can be effected by addition of a reducing agent followed by excess hydrofluoric acid. Tests showed that with chromous sulfate and stannous chloride as reducing agents, the reduction of uranium was complete in less than one hour at room temperature. With stannous fluoride, however, reduction was not complete in several hours. After addition of the reducing agent (either chromous chloride or chromous sulfate) to solutions having fluoride/zirconium mole ratio of 4.5 and uranium concentrations as high as 0.03 M, no precipitation of uranium tetrafluoride occurred on standing for four days or longer, even though the solubility of uranium tetrafluoride in these solutions was exceeded. However, the addition of excess hydrofluoric acid caused almost immediate precipitation.

Using the six-inch diameter stainless steel fluid-bed calciner, experiments were performed on the drying of simulated STR slurries containing 1.42 M zirconium, 5.8 M fluoride, and 0.007 M uranium (about 1 weight per cent alloy equivalent). In all the runs a side stream of either 49 per cent aqueous hydrofluoric acid or anhydrous hydrogen fluoride was introduced to the feed stream upstream from the spray nozzle.

The first series of runs was made with a side stream of anhydrous hydrogen fluoride, which was fed from a cylinder in a thermostatted water bath. A 20-foot coil of tubing was installed in the feed line subsequent to the junction of the hydrogen fluoride side stream. This coil provided a residence time of four minutes, at a flow rate of 90 milliliters per minute, to allow the uranium tetrafluoride precipitate to form.

There was one shortcoming to the use of anhydrous hydrogen fluoride. The flow rate of hydrogen fluoride was very sensitive to any pressure build-up subsequent to the side stream junction and the flow was occasionally interrupted. Also, it was noticed that the hydrogen fluoride gas was introduced into the feed line in pulses which completely displaced the liquid in the feed line. Although smooth operation was not achieved with the use of anhydrous hydrogen fluoride, eight runs were made. The bed temperature was 350 C and the feed flow rate ranged from 40 to 90 milliliters per minute. The quantity of hydrogen fluoride added depended upon the feed flow rate and was sufficient to increase the fluoride-zirconium
ratio from 4.5 to 10. Seven runs were terminated by either lumps in the bed or plugging within the nozzle. One run was satisfactory; this indicated that it was possible to operate the column successfully at a feed rate of 40 milliliters per minute and a bed temperature of 350°C. This run lasted four hours and was terminated by a leak in the feed line.

A screen analysis of the bed indicated that a large fraction of fines was produced. The fraction of -100 +200 mesh increased from 0.04 to 0.22. The fraction of -20 +40 mesh meanwhile decreased from 0.40 to 0.18. However, there seemed to be no tendency to produce particles which were -200 mesh in size. A previous run, ZP-4 (ANL-5820, page 58), showed a similar tendency to decrease the fraction of -20 +60 mesh and increase the fraction of -60 +200 mesh.

Because the anhydrous hydrogen fluoride stream entered the feed line in sporadic pulses, it was decided to utilize an aqueous hydrofluoric acid side stream. The aqueous hydrofluoric acid stream was pumped by displacement with carbon tetrachloride and was introduced into the main feed stream at a point about four feet from the nozzle. For this series of runs the feed rate was lowered to about 35 milliliters per minute. The effect of bed temperature was studied over the range from 300 to 460°C. Runs made at temperatures of 380 and 460°C were terminated by caking in the bed, specifically at the nozzle face. In these runs there was a tendency to form large particles (about 1/8- to 3/16-inch diameter) which were agglomerations of smaller particles.

Successful operation was achieved at a bed temperature of 300°C using an aqueous hydrofluoric acid side stream of 12 ml/min and a feed flow rate of 30 milliliters per minute. There was no change in particle size or distribution during the run which lasted six hours. The run was interrupted after three hours for overnight shutdown, and no difficulty was experienced in starting the run the following day. The run was terminated when the supply of zirconium-uranium feed solution became depleted after three additional hours. Samples of the final bed containing precipitated uranium tetrafluoride will be fluorinated in laboratory-scale equipment to determine the extent of uranium removal possible.

Similar experiments were carried out in the three-inch diameter Monel column using solutions with higher uranium concentrations, 0.03 M instead of 0.007 M. Uranium (VI) was added as uranyl fluoride, and stannous chloride was added to reduce the uranium to the tetravalent state.

A 3/8-inch OD plastic coil was installed in the feed line upstream from the spray nozzle. The coil furnished several minutes residence time for the uranium tetrafluoride precipitate to form after a side stream of 49 per cent aqueous hydrofluoric acid was added to the main feed stream. It was observed that precipitation occurred immediately
after the hydrofluoric acid and feed streams mixed. The particles of uranium tetrafluoride grew very rapidly and clogged both the spray nozzle and the coil. Even after the coil was eliminated and the two streams connected right at the nozzle, permitting only a very short time for precipitation to occur, plugging of the nozzle was encountered. Larger spray nozzles, 0.028-inch openings, instead of 0.020-inch openings are now being tested in the three-inch unit.

A number of additional runs were made in the three-inch unit to examine the drying characteristics of 15 M fluoride solutions with fluoride-to-zirconium mole ratio of 10. The variables studied included bed temperature, atomizing pressure and nozzle size. All of these tests resulted in the formation of cakes on the face of the nozzle, which often led to caking of the entire bed. This was not the case for solutions with fluoride-zirconium ratios of 4.5 and the difference in behavior is not understood. Zirconium fluoride hydrate systems have not been thoroughly studied. Microscopic examination of particles formed at different temperatures are being made in the hope they will furnish some clue to the nozzle cake formation. Also some experiments involving the use of a thermobalance are planned to provide information on the decomposition of hydrates of similar compounds.

2. Microscopic Study of Fluid-Bed Calcined Solids
(N. Levitz)

In order to try to understand the particle formation and/or growth of particles during fluid-bed calcining operations, a microscopic study of the various products was started. Samples of refined uranium trioxide and zirconyl fluoride were sieve analyzed and the separate fractions mounted in Lucite. The specimens were then polished and examined. Photographs of several of the samples are shown in Figure 7.

It was noted that there is a distinct difference between the two types of particles. The uranium trioxide formed during denitrification of uranyl nitrate is made up almost entirely of agglomerates, small particles cemented together, while the particles of zirconyl fluoride made by fluid-bed drying appear almost entirely as single particles. In each case the particles grow as a result of several passes through the spray zone before they are withdrawn in the product stream. The successive layers appear as concentric rings.

The percentage of agglomerates of uranium trioxide in the various fractions increased with increasing particle size, that is, the larger particles (plus 20 and 40 mesh) were practically all agglomerates while the minus 200 mesh fraction contained more single particles. The particles which formed the agglomerates were roughly 100 mesh. Also, the uranium trioxide particles contained large voids, apparently formed
FIGURE 7
PARTICLE GROWTH IN FLUID-BED CALCINED SOLIDS

-20 + 40 MESH 35X
(a) URANIUM TRIOXIDE

-100 + 200 MESH 100X
(b) URANIUM TRIOXIDE

-20 + 40 MESH 35X
(c) ZIRCONYL FLUORIDE

-60 + 100 MESH 35X
(d) ZIRCONYL FLUORIDE
by escaping gases. The fines produced by attrition or by calcination of spray droplets probably serve as nuclei for the intermediate particle size. The central nuclei appear to be roughly 50 microns in size. To augment this work, examination of the aluminum oxide from fluid bed calcination of aluminum nitrate is planned.

B. Calcination of Reactor Fuel Processing Wastes
(J. W. Loeding, R. Beck, C. Schoffstoll)

The fluidized-bed waste calcination process involves spray injection of liquid radioactive wastes into a heated, agitated bed of solid particles thereby converting the wastes to their constituent oxides. Emphasis has been directed toward the processing of ICPP waste, which is predominately aluminum nitrate with excess nitric acid, sodium and mercuric ions and fission product nitrates.

Work during this period has involved equipment modifications, the determination of non-volatile fission product activity in the gas, the efficacy of carbon monoxide in reducing ruthenium volatilization and providing internal heat generation, testing of the solid product at elevated temperatures to study the fission product volatilization behavior, and a bench-scale test of a new proposal for filter blowback.

1. Determination of Non-Volatile Fission Product Activity in Off-Gas

Three runs were made using feed diluted one part of ICPP waste to 100 parts of inactive solution, the highest activity level used thus far. All runs had the same feed composition and activity: 2.1 M Al(NO₃)₃, 1.25 M HNO₃, 0.15 M NaNO₃, 0.008 M Hg(NO₃)₂, gross beta 1.25 x 10⁷ cpm/ml, gross gamma 3.25 x 10⁵ cpm/ml, and ruthenium 2.25 x 10⁵ cpm/ml. One run (No. 42) differed in that carbon monoxide and nitrogen replaced air as the fluidizing gas and nitrogen replaced all other air (nozzle, purge, etc.). Operationally, all runs were excellent and voluntarily terminated. The data are shown in Table 6.

The more active feed employed in these runs allowed the demonstration of higher non-volatile fission product decontamination factors across the porous metal filters (5.8 x 10⁶). These non-volatile fission product decontamination factors were determined by taking a sizable (20 to 25 ml) aliquot of the condensate, heating with sulfuric acid and sodium bismuthate to volatilize the ruthenium, and counting the remainder of total γ counts. The residue was then scanned by a gamma-scintillation spectrometer which showed that the bulk of the activity was cesium-137 with traces of cerium-144. The amount of ruthenium in the condensate in Runs 40 and 41 was less than one per cent of the feed ruthenium. The amount of radioactivity remaining in the non-condensable off-gases during
Table 6
RESULTS OF WASTE CALCINATION RUNS

Feed Analysis, cpm/ml

<table>
<thead>
<tr>
<th>Feed</th>
<th>Gross $1.25 \times 10^7$</th>
<th>Gross $3.25 \times 10^5$</th>
<th>Ra $2.25 \times 10^5$ (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRC-40</td>
<td>Temp 500 C</td>
<td>Feed 95.1 ml/min</td>
<td>Fluid Gas-Air</td>
</tr>
<tr>
<td>HRC-41</td>
<td>Temp 500 C</td>
<td>Feed 95.1 ml/min</td>
<td>Fluid Gas-Air</td>
</tr>
<tr>
<td>HRC-42</td>
<td>Temp 550 C</td>
<td>Feed 95.1 ml/min</td>
<td>Fluid Gas CO + N$_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run Time (hr)</th>
<th>Total $\gamma$</th>
<th>Ra $\gamma$</th>
<th>% of Feed Ra</th>
<th>Total $\gamma^a$</th>
<th>Non-volatile</th>
<th>DF DF</th>
<th>Filter Sample Gross $\gamma$ (cpm/min of run time)</th>
<th>Gamma/min of run time (after Ra Removal)</th>
<th>% Feed Ra</th>
<th>DF for Non-Volatile PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRC-40</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.66 x 10$^3$</td>
<td>1.12 x 10$^7$</td>
<td>0.05</td>
<td>16</td>
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<td>1</td>
<td>6.6 x 10$^3$</td>
<td>4.6 x 10$^7$</td>
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<td>52</td>
<td>6.4 x 10$^3$</td>
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<td>2</td>
<td>1.15 x 10$^3$</td>
<td>1.02 x 10$^7$</td>
<td>0.5</td>
<td>77</td>
<td>4.5 x 10$^3$</td>
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<td>3</td>
<td>8.54 x 10$^3$</td>
<td>4.92 x 10$^7$</td>
<td>0.3</td>
<td>53</td>
<td>3.66 x 10$^3$</td>
<td>1.53 x 10$^3$</td>
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<td>HRC-41</td>
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<tr>
<td>0</td>
<td>1.68 x 10$^3$</td>
<td>9.37 x 10$^7$</td>
<td>0.4</td>
<td>80</td>
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<td>56</td>
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<td>2</td>
<td>1.52 x 10$^3$</td>
<td>1.8 x 10$^7$</td>
<td>0.5</td>
<td>79</td>
<td>4.2 x 10$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>1.52 x 10$^3$</td>
<td>1.3 x 10$^7$</td>
<td>0.5</td>
<td>114</td>
<td>1.3 x 10$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRC-42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>8.56 x 10$^3$</td>
<td>7.5 x 10$^7$</td>
<td>0.3</td>
<td>71</td>
<td>4.0 x 10$^3$</td>
<td>1.39 x 10$^3$</td>
<td>3.3 x 10$^3$</td>
<td>0.052</td>
<td>9.3 x 10$^3$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.46 x 10$^3$</td>
<td>5.8 x 10$^7$</td>
<td>0.7</td>
<td>259</td>
<td>9.0 x 10$^3$</td>
<td>6.9 x 10$^3$</td>
<td>83</td>
<td>0.0023</td>
<td>3.2 x 10$^3$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7.02 x 10$^3$</td>
<td>7.9 x 10$^7$</td>
<td>0.2</td>
<td>132</td>
<td>2.5 x 10$^3$</td>
<td></td>
<td>3.18</td>
<td>0.0004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.62 x 10$^3$</td>
<td>1.3 x 10$^7$</td>
<td>0.95</td>
<td>53</td>
<td>4.4 x 10$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Obtained by fuming to remove Ra by volatilization and counting for $\gamma$ activity. Samples then scanned - Cs and Eu found.

$^b$ Due to presence of metallic Ra in samples considerable fuming occurred during Ra analysis. Actual value may be somewhat higher.
Run 40 was less than in any previous run, both with respect to the ruthenium in the off-gas (≤0.05 per cent of feed ruthenium) and with respect to the non-volatile fission products (decontamination factor across the filter and condenser $2.5 \times 10^4$). These data were obtained by passing the off-gas through a filter paper, counting the total activity on the paper, then leaching the asbestos filter paper with hydrochloric acid, fuming to remove ruthenium, and counting the residue.

2. **Volatilization of Fission Products from Calcined Oxide at High Temperatures**

In an effort to determine the effect of temperatures higher than calciner operating temperatures on the volatilization of fission products from the calcined product, 1-gram samples of the product at 400 and 550 C were pulverized and ignited for 2 hours at temperatures of 700 C to 1200 C. Results may be seen in Table 7. No loss of activity within experimental error was observed below 1000 C. At 1200 C most of the gamma activity was lost due to cesium volatilization (loss of cesium as determined by gamma-scintillation spectrometer analysis was 99.9 per cent). Additional ignition tests will be performed at 1000 C on solid product produced at temperatures of 450, 500 and 550 C to verify the results obtained with 400 C product. The practical temperature limit of stored calcined fission product wastes containing cesium appears to be between 1000 and 1200 C. Heating at the higher temperature might be a means for intentional quantitative cesium removal.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Gross cpm/g before Ignition</th>
<th>Per Cent Loss of Activity on Ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>$3.74 \times 10^4$</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>$3.58 \times 10^4$</td>
<td>0</td>
</tr>
<tr>
<td>1200</td>
<td>$3.49 \times 10^4$</td>
<td>82.8</td>
</tr>
<tr>
<td>1200</td>
<td>$1.17 \times 10^7$</td>
<td>86.0</td>
</tr>
</tbody>
</table>

Product calcined at 400 C

Product calcined at 550 C
3. Use of Carbon Monoxide in Suppressing Ruthenium Volatilization

It was discovered subsequent to the first run using carbon monoxide as the fluidizing gas (No. 31) that the combination of high off-gas temperature (>700 C) plus the reducing atmosphere of carbon monoxide had caused the degradation of the porous stainless steel filters in the disengaging section. This necessitated the replacement of certain filters; however, an insufficient quantity of spare filters precluded the replacement of all filters at this time.

Inspection of the sintered filters following Run 42 revealed many cracks, some of which probably had as their origin the previously made carbon monoxide run (No. 31). An increasing state of filter decay might account for the decrease in non-volatile fission product decontamination factor noted in Run 41. The small amount of total gamma activity appearing in the off-gas stream from Run 42 despite the damaged filters can be explained by assuming the presence of a pre-coat of aluminum oxide on the filters in itself acting as an adequate filter. This would also explain the higher activity blank values obtained prior to each run, at a time when the filters were relatively clean. The values for both percentage of feed ruthenium appearing in the off-gas (<0.005 per cent) and the non-volatile fission product decontamination factor (3.2 x 10^6) in Run 42 are the best yet obtained. The amount of ruthenium in the condensate (one per cent of feed ruthenium) was similar to that in Runs 40 and 41, indicating that at high calcination temperatures carbon monoxide does not aid in further decreasing ruthenium volatilization. The condensate was about neutral, indicating the destruction of the oxides of nitrogen.

In Run 42 the desired effect of utilizing the heat of reaction in the bed was realized. Upon the addition of carbon monoxide to the bed at 550 C the temperature increased sharply to 620 C in the bed and to 770 C in the filter section. Input power requirements to maintain 550 C in the bed were reduced 20 per cent. All insulation was removed from the filter section, yet the temperature still exceeded 600 C, indicating a continuing reaction. No further carbon monoxide runs are planned in this equipment. The feasibility of the process in suppressing ruthenium volatilization at low calcination temperatures, destroying oxides of nitrogen, and supplying internal heat has been demonstrated.

4. Plugging Resistance Test of Sintered Metal Filters

A bench-scale experiment has been assembled to provide a long-term test of a proposed filter blowback system. A six-inch glass column containing a fluidized bed of aluminum oxide and two sintered stainless steel bayonet filters was assembled as shown in Figure 8. High pressure (100 psig) air controlled by cam-activated solenoid valves
is directed through nozzles in fractional second bursts through venturi-shaped fittings in the filter outlets. Each filter is blown back once per minute. This technique has allowed a build-up of a thin pre-coat of aluminum oxide fines which seems to prevent plugging of the porous metal. Pressure drop increase since start up has been about six inches of water, most of which occurred in the first few hours. No measurable increase has been noted during the last month, even though attrition in the bed has resulted in a considerable increase in the amount of fines present. Operating variables (except for temperature) are similar to those in the active calciner.

5. Equipment Modification

Major equipment changes have been made since the last series of active runs in order to test proposed components for the plant-scale calciner being designed by Fluor Corp. for the ICPP. A venturi scrubber and a silica gel adsorber have been installed in the off-gas system. The venturi scrubber is being considered for plant installation for the removal of particulate dust not removed by primary cyclone separators. The silica gel adsorber is intended to remove ruthenium from the off-gas. Operation of these units will be tested in the pilot-scale calciner with feed containing tracer ruthenium and ICPP waste.

6. Treatment of Calcined Waste Oxide
   (I. Knudsen)

Two areas in which an improvement in the characteristics of the calcined waste oxide may simplify storage requirements are, first, the reduction of leachability of the radioactive fission products and, second, improvement of the low thermal conductivity. Elimination of the need for protection from the elements and of the decay-heat dissipation limitation on surface-to-volume ratio might permit storage in excavations or caverns with only nominal container costs.
Reduction in water leachability of the oxide may be achieved by coating with an impervious material such as a ceramic glaze. Current work has attained limited success in coating of the particles in a hot fluidized bed by spraying in a dilute slurry (5 weight per cent) of a low-temperature glaze; however, maturing of the coating by firing in a furnace at the proper temperature has not produced the vitreous surface desired. This is apparently due to the reaction of the alumina particles with the glaze, forming a refractory mass. Parmelee\textsuperscript{2} recommends the use of high-temperature glazes on alumina bodies; therefore, coatings maturing at temperatures of 1100 to 1300 C are being tested to determine whether or not it is possible to get an impervious coating without applying an excessive amount of glaze.

Some study has been made of the feasibility of improving the heat-transfer characteristics of the oxide by compacting with powdered metal. A wide range of compositions and components have been reported in the literature; treatment of the mixtures consists of hot pressing, or cold pressing and sintering at temperatures above 1500 C, apparently to obtain high mechanical strength. Only one thermal conductivity figure has been found, reporting a 15 per cent increase above that of uranium dioxide for a 20 to 80 mixture of zirconium-uranium dioxide.\textsuperscript{3} The small increase was attributed to the poor thermal conductivity of the zirconium. Further literature studies will be made of this procedure and variations of it.

C. Fluorination of Uranium Tetrafluoride in a Fluid-Bed Reactor
(G. J. Vogel, L. Marek, A. Rashinskas)

In the previous report (ANL-5820, page 65) was summarized the results of preliminary fluorination runs on refined green salt, and on Anaconda acid-leach green salt in the 2.5-inch diameter fluid-bed fluorinator. These runs served primarily to define satisfactory operating conditions for continuous feed with no solid diluent in the bed. With refined feed, smooth operation without caking was found for operation between 300 and 450 C. Additional runs with refined uranium were made in order to determine the dependence of fluorine utilization and uranium hexafluoride production rate upon the major process variables, such as temperature, bed conditions, and fluidizing gas conditions. These data showed a maximum fluorine efficiency of 91 per cent at 450 C. In addition, one run was made with Anaconda acid-leach green salt.


\textsuperscript{3} Rauch, W. G., ANL-5628 (August, 1954).
1. **Equipment**

A schematic of the equipment used in the current runs was presented in Figure 10, ANL-5789, page 39. The fluid-bed reactor was 2½ inches in diameter, topped by a 6-inch diameter disengaging section. The bottom distributor contained 24 inverted cone holes with 1/16-inch openings at the tip of the cone. The bed cross-section was 0.0332 sq. ft.

Heat was supplied by clamshell Nichrome wire heaters. Six inside and five outside skin thermocouples were provided. In early runs variable voltage transformers were used for control, but difficulty in smooth control was encountered in operation at the lower temperatures and bed heights. Subsequently, automatic control was installed with improved smoothness of operation. No means of cooling was provided in these runs other than normal heat losses.

Fluorine and nitrogen flows were measured by orifice-pressure gage systems. In addition, the fluorine flow was determined by pressure drop in a 17.6-cu ft metering tank. Both flows were regulated by automatic flow-control valves. A fluidizing gas preheater was provided.

Uranium tetrafluoride was fed directly into the bed by a one-inch screw controlled by a variable speed drive. The rate of powder feed could be determined by observing the change in level in a Fluorothene sight glass.

The off-gas from the reactor was put through two filter units. These filters, equipped for blowback, were of Monel bayonet type with 10-micron porosity. After passing through the filter, the uranium hexafluoride in the off-gas was condensed in a 10-ft long, 3-in. diameter condenser of a finned-tube type. Twelve fins, parallel to the tube axis, were mounted on the 3/4-in. tubing through which trichloroethylene coolant was circulated. A 3-hp refrigerator operating on Freon-12 was the primary cooling unit. The trichloroethylene was steam heated to melt the uranium hexafluoride for product removal. The condenser was located on a scale to allow measurement of the rate of product collection.

2. **Procedure**

Preliminary data on pressure drop and fluidization characteristics of the various green salts and calcium fluoride were first obtained in a glass column using air as a fluidizing medium.

Start-up of actual fluorination runs was begun by passing sufficient nitrogen through the reactor to fluidize the feed. The uranium tetrafluoride was then screw-fed into the reactor until the desired bed
height was obtained. When the bed had been heated to temperature, the fluorine was introduced. In the runs reported here, the fluidizing gas was not preheated before entry to the bed. The rate of uranium hexafluoride production was determined by reading the scale at 5-minute intervals. A run consisted usually of operating for two hours at equilibrium conditions.

3. Results

Fluorine efficiency studies were made on two types of materials: the refined green salt and the Anaconda acid-leach ore concentrate. With refined uranium tetrafluoride the effect on fluorine efficiency of changes in bed height, fluorine concentration, fluidizing gas velocity, temperature, and bed diluent has been determined. Fluorine efficiency, or fluorine utilization, was calculated as fluorine in product uranium hexafluoride divided by fluorine entering bed in fluidizing gas.

Data from several runs are given in Table 8, showing the effect of process variables on fluorine efficiency and production rate.

### Table 3

**Fluid-Bed Fluorination of Uranium Tetrafluoride: Effect of Temperature, Fluorine Concentration, and Bed Diluent**

<table>
<thead>
<tr>
<th>UF₆ Feed</th>
<th>Temp (C)</th>
<th>F₂ Conc (%)</th>
<th>Bed Diluent (% CaF₂)</th>
<th>Bed Ht/Dia</th>
<th>Fluorine Efficiency (%)</th>
<th>UF₆ Prod Rate (lb/(hr)(sq ft))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refined</td>
<td>300</td>
<td>30</td>
<td>0</td>
<td>4.4</td>
<td>29</td>
<td>73</td>
</tr>
<tr>
<td>Refined</td>
<td>350</td>
<td>30</td>
<td>0</td>
<td>4.4</td>
<td>67</td>
<td>166</td>
</tr>
<tr>
<td>Refined</td>
<td>400</td>
<td>30</td>
<td>0</td>
<td>4.4</td>
<td>85</td>
<td>193</td>
</tr>
<tr>
<td>Refined</td>
<td>450</td>
<td>30</td>
<td>0</td>
<td>4.4</td>
<td>91</td>
<td>194</td>
</tr>
<tr>
<td>Refined</td>
<td>350</td>
<td>14.9</td>
<td>0</td>
<td>4.4</td>
<td>63</td>
<td>76</td>
</tr>
<tr>
<td>Refined</td>
<td>350</td>
<td>8.6</td>
<td>0</td>
<td>4.4</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>Refined</td>
<td>400</td>
<td>30</td>
<td>50</td>
<td>3.4</td>
<td>38</td>
<td>86</td>
</tr>
<tr>
<td>Refined</td>
<td>400</td>
<td>30</td>
<td>85</td>
<td>3.4</td>
<td>33</td>
<td>64</td>
</tr>
<tr>
<td>Refined</td>
<td>450</td>
<td>30</td>
<td>85</td>
<td>3.4</td>
<td>54</td>
<td>121</td>
</tr>
<tr>
<td>Anaconda Acid Leach</td>
<td>450</td>
<td>30</td>
<td>85</td>
<td>4.0</td>
<td>51</td>
<td>114</td>
</tr>
</tbody>
</table>

The relative magnitudes of effects on fluorine efficiency are also shown graphically by a plot of the data in Figure 9. Temperature had a pronounced effect and fluorine concentration a rather small effect on fluorine efficiency. At the 400 C temperature, 43 per cent fluorine in nitrogen was above the
The maximum fluorine concentration that could be tolerated, due to limitations of heat removal in this unit. The effects of bed height and superficial gas velocity on fluorine efficiency are shown in Tables 9 and 10.

The addition of an inert diluent, calcium fluoride, to the bed decreased the fluorine efficiency markedly, as shown in Table 8 and Figure 9. The fluorine efficiencies were approximately halved by additions of 50 to 80 per cent diluent to refined uranium tetrafluoride. With 85 per cent bed diluent, approximately the same fluorine efficiencies were obtained for Anaconda acid-leached and for refined green salt. Typical size analyses of various feeds are given in Table 11.

A ratio of expanded bed height to diameter of about 5 was used in most of the tests because of ease of operation. (The ratio is somewhat higher than usual in commercial fluid-bed reactors.) Higher height to diameter ratios give higher fluorine efficiencies, as shown by the data in Table 9. These data also imply proportionately lower reactivity for the
### Table 9
**Effect of Bed Height on Fluorine Efficiency**

<table>
<thead>
<tr>
<th>Bed Height Diameter</th>
<th>Fluorine Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>14</td>
</tr>
<tr>
<td>3.2</td>
<td>36</td>
</tr>
<tr>
<td>4.3</td>
<td>68</td>
</tr>
<tr>
<td>5.4</td>
<td>80</td>
</tr>
</tbody>
</table>

Conditions: Temperature 350 C  
Fluorine Conc 30%  
Superficial  
Gas Velocity 0.5 ft/sec

### Table 10
**Effect of Gas Velocity on Fluorine Efficiency**

<table>
<thead>
<tr>
<th>Superficial Gas Velocity ft/sec</th>
<th>Fluorine Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>85</td>
</tr>
<tr>
<td>0.42</td>
<td>77*</td>
</tr>
<tr>
<td>0.53</td>
<td>86</td>
</tr>
</tbody>
</table>

Conditions: Temperature: 400 C  
Feed: Refined UF₄  
Bed Height: 4.5  
Diameter:  
Fluorine Conc: in inlet gas: 30%

*Some sintering of green salt in this run

### Table 11
**Physical Properties of Green Salt**

<table>
<thead>
<tr>
<th>Green Salt</th>
<th>Pack Density, g/cc</th>
<th>+20</th>
<th>-20 to +40</th>
<th>-60 to +60</th>
<th>-60 to +100</th>
<th>-100 to +200</th>
<th>-200 to +325</th>
<th>-325</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rand Ore</td>
<td>1.6</td>
<td>0.1</td>
<td>46</td>
<td>29</td>
<td>14.0</td>
<td>8.0</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Anaconda Acid Leach</td>
<td>2.7</td>
<td>0.20</td>
<td>0.1</td>
<td>7.6</td>
<td>25</td>
<td>36</td>
<td>24</td>
<td>6.8</td>
</tr>
<tr>
<td>Anaconda Carbonate Leach</td>
<td>2.7</td>
<td>0.05</td>
<td>6.4</td>
<td>26</td>
<td>31</td>
<td>32</td>
<td>12</td>
<td>0.9</td>
</tr>
<tr>
<td>Refined Green Salt*</td>
<td>3.5</td>
<td>0.02</td>
<td>6.9</td>
<td>36</td>
<td>34</td>
<td>20</td>
<td>3.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcium Fluoride Diluent</td>
<td>0</td>
<td>7</td>
<td>35</td>
<td>20</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Bulk density 3.2
shorter bed heights. This is probably due, at least in part, to lower bed temperatures near the point of entry of relatively cool fluidizing gas. Only the bottom one inch or so of the bed is so affected.

Variation of fluidizing gas velocity in the range from 0.34 to 0.53 ft/sec had no appreciable effect on fluorine efficiency, as shown in Table 10. These data were obtained with refined uranium tetrafluoride and no diluent in the bed.

4. Program

A study of the fluorination of green salt from Rand ore concentrate is under way.

D. Mixing Studies in Straight and Tapered Fluidized Beds
(H. Littman)

Studies have been initiated on the comparison of fluidization in straight and in tapered columns based on work\(^4\) in which it was shown that batch contactors are strikingly more efficient than continuous contactors for the production of uranium tetrafluoride. The high rate of solids mixing in fluidized beds lowers concentration gradients in the bed by mixing highly converted material at the product outlet with poorly converted material at the feed inlet. It is claimed that tapered columns have lower mixing coefficients which should allow deeper beds of excellent stability and higher productivity.

Qualitative Studies

Qualitative studies of the solids mixing in a straight and in a tapered fluidized bed have been performed by watching colored glass beads diffuse into a bed of colorless ones in a 2-inch ID "Lucite" column. In the straight column mixing was rapid, as expected. In the tapered column the mixing could be made as rapid as that in the untapered column or suspended so that no solids mixing could be observed at all. The mixing increases with increasing flow rate of the fluidizing gas.

The solids flow pattern in the tapered bed is markedly different from that in an untapered bed; that is, the solids appear to be pulsed upward and downward in small mixing segments with transfer of particles between segments, whereas the flow pattern is upward and outward in the center of the bed and downward at the walls in an untapered bed. The gas flows through the tapered bed smoothly, with mild bubbling at the higher gas flow rates. Under similar conditions, vigorous bubbling occurs in the bed of an untapered column.

\(^4\)Levey, R. P., Jr., "A New Type of Gas-Solids Contactor for UF\(_4\)
Quantitative Studies

Based on the qualitative studies, measurement of the solids mixing coefficient in a fluidized bed using the pulse-tracer technique has been undertaken. The basis of the method and the experimental equipment being assembled is described below. The mathematical analysis is the same whether a tapered or an untapered column is used.

Consider a bed of fluidized solids to which a very small amount (or pulse) of particles, identical to those in the bed except that they are radioactive, is added at the top.

The tracer solids travel downward through the column and eventually become mixed homogeneously in the bed.

It can be shown that the concentration of tracer \( C \) at any level \( x \) at any time \( t \) is represented by the diffusion equation

\[
\frac{\partial C(x,t)}{\partial t} = M \frac{\partial^2 C(x,t)}{\partial x^2},
\]

where \( M \) is defined as the mixing coefficient.

Solving the diffusion equation with the appropriate boundary conditions, the result is:

\[
C(x,t) = C_\infty + 2 \frac{C_0}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \left[ \sin \left( \frac{n\pi}{L}x \right) \right] \left[ \cos \left( \frac{n\pi}{L}x \right) \right] e^{-M\left(\frac{n\pi}{L}\right)^2 t} \tag{2}
\]

If \( x \) is very small compared to \( L \), that is, a small amount of tracer is added to the bed the equation becomes:

\[
\frac{C(x,t)}{C_\infty} = 1 + 2 \sum_{n=1}^{\infty} \left[ \cos \left( \frac{n\pi}{L}x \right) \right] e^{-M\left(\frac{n\pi}{L}\right)^2 t} \tag{3}
\]

The left side of equation (3) represents the tracer concentration at any level at any time compared to the tracer concentration after an infinite time. When the tracer is homogeneously mixed in the bed, \( \frac{C(x,t)}{C_\infty} = 1 \).

The right hand side of the equation is composed of a space part, \( \cos \frac{n\pi x}{L} \), and a time part, \( e^{-M\left(\frac{n\pi}{L}\right)^2 t} \). When the observation point is fixed (the location of the counter), the space part takes a definite value. Thus if the counter is placed at height \( x \) and the counts from the tracer recorded as a function of time, equation (2) can be used to calculate the mixing coefficient, \( M \). The process can be repeated for different counter locations to check whether \( M \) is a constant as assumed in the location of the diffusion equation.
If no correlation is obtained between the measured concentrations and those calculated using any M, it is apparent that the diffusion equation does not properly apply to the system.

Experimental

The column is 50 inches high and made of aluminum. The inlet is a two-inch square and the outlet rectangular, its dimensions depending on the taper used. The column is assembled from four machined plates, two of which are always the same and two of which can be adjusted to the desired taper.

A scintillation counter with a sodium iodide crystal is used to determine the tracer concentration in the column by gamma counting. The counter consists of the crystal photomultiplier tube, preamplifier, amplifier and scaler.

Copper beads (100-micron size) and three sizes of glass beads (25, 500 and 840-micron size) have thus far been obtained for use as bed materials. Glass and copper beads were irradiated in the pile to test residual activity and the uniformity of activation of individual particles. Both the copper and glass beads showed no residual activities, the copper decaying with a 12.8-hour half-life and the glass with the 15.0-hour sodium half-life. The uniformity of activation of the glass beads was good and the average deviation (in cpm/mg) for 10 particles taken at random was about 5 per cent. The copper beads have not been tested for uniformity of activations as yet.

A tracer with a relatively short half-life is desirable because of the obvious difficulty of separating the activated particles from the bed. The half-life should not be so short as to give an appreciable change in activity during the experiment. Copper-64 and sodium-24 are suitable tracers for the mixing studies.
A. Metal Oxidation-Ignition

The efforts to clarify the factors involved in the pyrophoricity of reactor materials are proceeding satisfactorily. The effects of many additives to uranium have been studied in oxygen. Current efforts have developed a relationship between the ignition temperature and the area-to-mass ratio or specific area. An experiment has been conducted to demonstrate that a small piece of uranium (large specific area) may serve as an igniter for the bulk metal. Several gas variables are being examined. Preliminary studies in air and mixtures of nitrogen and air have shown a complex behavior which will require further study. The variable due to the unknown reactivity of nitrogen has been eliminated by studying helium-oxygen mixtures. Between 33 and 60 volume per cent helium, the ignition temperature increases uniformly from 615 to 955°C. No ignition was observed in 80 per cent helium. The influence of moisture content on the ignition characteristics of uranium in the various atmospheres is under investigation.

Isothermal oxidation studies of uranium have been directed toward understanding the mechanism of oxidation which proceeds in two stages and attempting correlation with ignition test results.

A new procedure to test the ignition characteristics of zirconium has not yielded satisfactorily reproducible results. Another procedure using foils initially shielded by a helium atmosphere indicates probable reproducibility of 10 degrees if many samples are used to bracket the ignition temperature.

Isothermal oxidation studies of zirconium alloys are continuing. A series of experiments has been completed on Zircaloy-3 with varied heat treatments. All tests indicated no effect of the varied heat treatment on the oxidation characteristics. The oxidation prior to breakaway is only slightly faster than that for crystal bar zirconium.

A literature survey on the oxidation of plutonium metal has been completed.

1. Uranium Ignition Studies

The time-temperature burning curve approach used to test directly the susceptibility to ignition of uranium and its alloys has been described in previous quarterly reports, ANL-5759, 5789, and 5820. In the last report the burning curves and ignition temperatures were
presented for three sources of uranium, three metallurgical treatments and three concentrations (0.5, 1.0, and 2.0 atom per cent) of each of the following additives to uranium: aluminum, niobium, silicon, molybdenum, carbon, ruthenium, beryllium, zirconium, iron, and copper. In addition, three concentrations (0.05, 0.10, and 0.35 atom per cent) of hydrogen and four very low concentrations of aluminum were presented.

As was reported, uranium did not ignite in carbon dioxide. No appreciable reaction occurred until the sample was heated over 850 C.

Studies have been directed toward determining the effect of other gas variables and the sample size dependence.

a. Dependence upon Specific Area

Burning curves on various size and shape samples of uranium showed clearly a decrease of ignition temperature with a decrease of size. Data are presented in Table 12. A linear relationship was found between the logarithm of the reciprocal of the specific area (square centimeters surface per gram of sample) and the reciprocal of absolute temperature of ignition (see Figure 10).

\[
\log \left( \frac{1}{\text{Spec Area}} \right) = 5.231 - \frac{4190}{T} - \frac{19200}{RT}
\]

or

\[
\frac{1}{\text{Spec Area}} = 1.7 \times 10^4 e^{-\frac{RT}{19200}}
\]

Table 12

<table>
<thead>
<tr>
<th>Dimensions (mm)</th>
<th>Sample Shape</th>
<th>Source</th>
<th>Weight (g)</th>
<th>Specific Area (sq cm/g)</th>
<th>Ignition Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 x 12.5 x 8</td>
<td>Block</td>
<td>B base</td>
<td>34.2</td>
<td>0.280</td>
<td>640</td>
</tr>
<tr>
<td>10 x 10 x 10</td>
<td>Cube</td>
<td>A base</td>
<td>17.6</td>
<td>0.314</td>
<td>615</td>
</tr>
<tr>
<td>8.5 x 8.5 x 8.5</td>
<td>Cube</td>
<td>A base</td>
<td>11.1</td>
<td>0.396</td>
<td>595</td>
</tr>
<tr>
<td>8.5 x 8.5 x 8.5</td>
<td>Cube</td>
<td>Elect pur</td>
<td>11.1</td>
<td>0.396</td>
<td>595</td>
</tr>
<tr>
<td>3.5 x 3.5 x 3.5</td>
<td>Bar</td>
<td>B base</td>
<td>3.23</td>
<td>0.79</td>
<td>540</td>
</tr>
<tr>
<td>3.5 x 3.5 x 3.5</td>
<td>Cube</td>
<td>B base</td>
<td>0.690</td>
<td>1.04</td>
<td>550</td>
</tr>
<tr>
<td>0.45 x 0.3 x 0.7</td>
<td>Sheet</td>
<td>A base</td>
<td>0.656</td>
<td>2.63</td>
<td>470</td>
</tr>
<tr>
<td>0.24 x 0.14 x 0.14</td>
<td>Foil</td>
<td>B base</td>
<td>0.807</td>
<td>4.68</td>
<td>385</td>
</tr>
<tr>
<td>0.22 x 0.1 x 0.1</td>
<td>Foil</td>
<td>c</td>
<td>0.412</td>
<td>5.35</td>
<td>385</td>
</tr>
<tr>
<td>0.13 x 0.1 x 0.13</td>
<td>Foil</td>
<td>B base</td>
<td>0.408</td>
<td>8.50</td>
<td>380</td>
</tr>
<tr>
<td>0.05 x 0.01 x 0.015</td>
<td>Foil</td>
<td>c</td>
<td>0.077</td>
<td>49.0</td>
<td>335</td>
</tr>
<tr>
<td>0.03 x 0.02 x 0.025</td>
<td>Foil Chips</td>
<td>c</td>
<td>0.172</td>
<td>49.6</td>
<td>315</td>
</tr>
</tbody>
</table>

a. The reactor-grade uranium used for isothermal studies is called A base.

b. Determined by intercept method on burning curve in flowing oxygen with programmed furnace temperature increase of 10 degrees per minute.

c. Foil of undetermined purity, neither base metal.
The region of deviation from the straight line where ignition temperatures are just under 400°C is felt to be caused by the hump (maximum at 550°C) observed in the larger sample burning curve of B base* uranium (see ANL-5820, Figure 13, page 68). The tendency of the B base uranium sample temperature to increase more rapidly between 350 and 450°C may cause self heating, the sample temperature thus exceeding the real ignition temperature and causing ignition.

*The reactor-grade uranium used for isothermal studies is called A base. The uranium used by Battelle Memorial Institute to produce the series of alloys is called B base.
The graphical method of obtaining the ignition temperature (see ANL-5789, page 58) cannot distinguish, therefore, between the beginning of the hump and the initiation of ignition. If the sample size is just large enough to cause an ignition temperature higher than the maximum of the hump, the temperature will decrease, causing the hump in the temperature trace. As the increasing furnace temperature and self heating subsequently cause the ignition temperature to be exceeded, ignition will occur. Further study of the factors causing the hump in the burning curve are needed.

In the burning curve method, the sample temperature increases because the heat of reaction exceeds the heat loss from the sample. Although very little is known about the rate of heat loss in such a situation, it would not be expected to change markedly from run to run, at least in these controlled studies. The rate of self heating of the sample is a function of the reaction rate and the area. It would seem reasonable that ignition would occur when the rate of reaction exceeded some critical value. The measurement of such a fast rate is complicated and difficult. The relationship between the specific area and ignition temperature might be, therefore, the desired means for understanding mechanism or kinetics of the reaction. The reciprocal of specific area should be proportional to this proposed critical rate. Figure 10 would then be considered an Arrhenius plot, the slope of which would indicate an activation energy of 19.2 kcal/mole. This value is, perhaps coincidentally, identical with the activation energy determined by least squares for isothermal data for second-stage oxidation of uranium in 800 mm pressure oxygen over the temperature range 125 through 295 C (19.3 ± 0.6 kcal/mole). It is interesting to speculate whether or not this means that the reaction and the mechanism are the same in the region of ignition temperatures as at the lower temperatures in isothermal studies.

b. Bulk-Metal Ignition by Foil

An experiment was performed to confirm suspicious that the smallest piece of an aggregate of uranium chunks would serve as an igniter for large pieces. A sample of 0.25-mm (10-mil) foil, approximately one centimeter square, was placed on top of a B base uranium cube, 8.5 mm on an edge, and subjected to the programmed burning test. Two distinct and separate ignitions were observed visually. The foil ignited at 400 C, the same temperature as if it were alone, and the heat of its ignition was sufficient to cause the large cube to self heat rapidly and ignite.

c. Inductively Heated Ignition

It was of interest to determine the relative importance of the effect of the furnace temperature on the sustained burning after ignition. An ignition was initiated by admitting oxygen after inductively heating a sample in helium. As soon as the recorded sample temperature began to climb rapidly, indicating ignition, the power to the induction coil was turned off. Despite the fact that the surroundings were then cool, the sample
continued to burn rapidly with intense light emission until helium was used to replace the oxygen stream. This experiment would indicate that, once ignition has occurred, the temperature of the surroundings is not an important variable in the burning curve experiments.

d. Gas Variables

In order to understand clearly the complex behavior shown by burning curves in air, information was needed about the dependence on the flow rate of gas, the oxygen concentration and the partial reactivity of nitrogen diluent.

Variations of the flow rate of oxygen from 1000 to 3000 cc/min neither altered the shape of the burning curve nor changed the ignition temperature of pure uranium.

The problem of unknown reactivity of nitrogen was resolved by initially studying variation of oxygen concentration in helium mixtures. The series of burning curves presented in Figure 11 was conducted on 8.5-mm cubes of B base uranium in the tabulated mixtures of helium and oxygen.
It was observed that 33 per cent helium does not change the ignition temperature appreciably, but that the reaction proceeds more slowly as evidenced by the slow $\beta - \gamma$ transformation. Concentrations of helium from 33 to 60 per cent caused a uniform increase of ignition temperature, from 615 to 955 C (10 to 15 degrees/per cent helium). No ignition was observed in 80 per cent helium. Uranium might be subject to ignition in 80 per cent helium if the sample was heated over 1000 C.

Preliminary studies of uranium ignition in mixtures of nitrogen, and oxygen, including air, have shown a complex behavior which will require further study. The additional variable of water content of the gas is similarly being investigated.

2. Uranium Isothermal Studies

Experiments are under way in the Stanton Thermobalance to determine the influence of gas variables on the isothermal oxidation kinetics. The initial efforts are directed toward understanding the effects of mixtures of gases to simulate air, including the influence of moisture content.

Because of the low ignition temperatures observed for aluminum additives to uranium (370 C), it was hoped that isothermal rate determination could be accomplished at reasonable temperatures. Such studies might then be used to determine the fundamental kinetics and the influence of additives leading to ignition. Oxidation of the 1.00 atom per cent aluminum-uranium sample at 295 C in 200 mm oxygen has shown no great difference in the kinetics of reaction compared to pure uranium. The characteristic data are compared in Table 13. It appears that still higher temperatures will be needed to establish any correlation of isothermal oxidation rate and ignition temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st Stage Rate ((\mu g/(sq \text{ cm})(\text{min})))</th>
<th>Break Weight ((\mu g/sq \text{ cm}))</th>
<th>Break Time (min)</th>
<th>2nd Stage Rate ((\mu g/(sq \text{ cm})(\text{min})))</th>
<th>Maximum</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base-line Avg</td>
<td>10.2 ± 3.3</td>
<td>173 ± 38</td>
<td>19 ± 3</td>
<td>70.7 ± 2.4</td>
<td>53.0 ± 7</td>
<td></td>
</tr>
<tr>
<td>1 Atom Per Cent Aluminum - Uranium</td>
<td>11.1</td>
<td>82</td>
<td>8</td>
<td>97.8</td>
<td>43.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 13

COMPARISON OF RATES OF OXIDATION AT 295 C AND 200 mm OXYGEN FOR 1.00 ATOM PER CENT ALUMINUM IN URANIUM AND BASE-LINE DATA
3. **Zirconium Ignition Tests**

Studies are proceeding to find a method which will yield reproducible ignition temperatures for zirconium and zirconium alloys. The "burning curve" method, used successfully in the case of uranium, was tried and was found not to be applicable for zirconium. A very protective oxide is formed when zirconium is heated at low temperatures and the bulk metal would not ignite in this type of test even when heated above 1300 °C in an oxygen atmosphere.

A second type of test was studied in which the zirconium sample, mounted on a thermocouple, was plunged into a hot furnace with an atmosphere of flowing oxygen. Some degree of success has been obtained in correlating ignition with furnace temperature. However, thus far it has not been possible to obtain reproducible ignition temperatures as measured by inflections in the time-temperature traces.

A third approach, which at present appears to be the most promising, is a shielded type of ignition test. The test specimen is heated to a predetermined temperature in a helium atmosphere and then oxygen is admitted. Initial results indicate that by this method ignition temperatures may be defined within ±10 degrees °C if many runs are made to bracket the ignition temperature. Further ignition tests are proceeding on bulk and foil samples in oxygen and in air.

4. **Zirconium Isothermal Oxidation**

   a. **Oxidation of Alloys**

   Studies of the isothermal oxidation kinetics of zirconium-base binary alloys at 700 °C in 200 mm pressure oxygen are continuing. Correlation of the initial cubic rate constant and the "breakaway" phenomena will be attempted with respect to additive valence, oxide solubilities in zirconium dioxide, steric effects, additive concentrations, etc.

   b. **Zircaloy-3**

   Some further oxidation tests have been made on 0.025-in. thick Zircaloy-3 strip stock. Previous work on Zircaloy-3 has been reported in ANL-5820, pages 82 to 85.

   The results of these additional tests are summarized in Table 14. Run 13, on specimen No. 4 was carried out for 2600 minutes at 700 °C in dry air. This run was extended past the usual run length to study the reaction behavior after the breakaway. The oxidation initially obeyed the usual cubic rate law, but, after about 900 minutes, the breakaway
occurred and an accelerating oxidation took place. At about 2000 minutes the accelerating behavior stopped and a linear rate of 6.7 μg/(sq cm)(min) was followed until the end of the run. This run is illustrated in Figure 12. Also shown in this figure are a run on Zircaloy-3 at 400 C and a run on pure zirconium at 700 C. The 400 C run was carried out for three days (4320 minutes). The cubic rate law was followed throughout the run and the total weight gain was found to be 201 μg/sq cm. By extrapolation of the 400 C data it would take about 11.3 years before the total weight gain at 400 C reached 2246 μg/sq cm, the average weight at which breakaways were observed at 700 C.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>4</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, C</td>
<td>700</td>
<td>400</td>
<td>700</td>
</tr>
<tr>
<td>Sample</td>
<td>Zr-Crystal Bar</td>
<td>Zircaloy-3 No. 7</td>
<td>Zircaloy-3, No. 4</td>
</tr>
<tr>
<td>Sample Dimensions (inches)</td>
<td>0.39 x 0.39 x 0.59</td>
<td>0.63 x 1.5 x 0.025</td>
<td>0.63 x 1.0 x 0.025</td>
</tr>
<tr>
<td>Slope(^a) of Log-Log Plot (1/n)</td>
<td>0.36</td>
<td>0.34</td>
<td>0.30</td>
</tr>
<tr>
<td>Cubic Rate Constant,(^a) ( k ) (μg(^3) cm(^{-6}) min(^{-1}))</td>
<td>(0.97 \times 10^7)</td>
<td>(1.9 \times 10^3)</td>
<td>(1.1 \times 10^7)</td>
</tr>
<tr>
<td>Breakaway Time (min)</td>
<td>-</td>
<td>-</td>
<td>870</td>
</tr>
<tr>
<td>Breakaway Weight (μg/sq cm)</td>
<td>-</td>
<td>-</td>
<td>2225</td>
</tr>
<tr>
<td>Total Length of Run (min)</td>
<td>1400</td>
<td>4320</td>
<td>2600</td>
</tr>
<tr>
<td>Total Weight Gain (μg/sq cm)</td>
<td>2392</td>
<td>201</td>
<td>9769</td>
</tr>
</tbody>
</table>

\(^a\)For samples exhibiting breakaway oxidation phenomena, this term applies only to the oxidation before the breakaway.

The appearance of the Zircaloy-3 specimens after the runs varied with the temperature and the length of the runs. After 4320 minutes at 400 C, the specimen was covered with a thin, adherent, dark gray film, and there was no visible evidence that any dimensional change had taken place. The specimens oxidized at 700 C for 1400 to 1600 minutes produced
a blue-black surface film in which cracks were evident. Along the crack boundaries and on the edges of the samples a tan color was observed. The specimens also showed slight curvature. The specimen which was run for 2600 minutes at 700 C had a cracked, tan-colored layer all over the surface and along the edges. It also showed a very definite curvature.

**FIGURE 12**

Oxidation of Zircaloy-3 and Zirconium in Dry Air

All oxidation tests on Zircaloy indicated that the oxidation reaction kinetics in air are independent of the fabrication procedure. The cubic rate constant for the oxidation of Zircaloy prior to breakaway was only slightly higher than that for the crystal bar zirconium and slightly lower than that for sponge zirconium. After oxidation of Zircaloy-3 at 700 C in air to 2250 ± 60 μg/cm the breakaway phenomena occurred. No breakaway was observed for pure zirconium.
5. **Plutonium Oxidation—Literature Survey**

Preparations are underway to study the oxidation and ignition characteristics of plutonium. A survey of the literature has revealed that relatively few studies have been made of the reactions of plutonium metal in air, nitrogen, and carbon dioxide. There are apparently no data available on the reaction in pure oxygen and the studies of the reaction in air and other gaseous media are not detailed investigations.

**B. Metal-Water Reactions**

(L. Baker, C. H. Smith, W. A. Rodger, R. C. Vogel)

There is considerable concern over the potential heat release caused by the reaction of the core materials of a nuclear reactor with water or steam in the event of an accident. Two types of reactor accidents leading to metal-water reactions are generally considered to be the most serious: (1) the loss-of-coolant accident, and (2) the power excursion accident. Either causes the reactor core materials, such as zirconium, aluminum, stainless steel, uranium and their alloys, to overheat, possibly melt or even vaporize. Rapid dispersal of the metals into the reactor cooling water might then lead to a violent chemical reaction. Energy considerations indicate that the heat released by such chemical reactions can be greater than the nuclear heat release. It was, therefore, decided to begin a study of metal-water reactions at high temperatures.

A literature survey of molten metal-water reactions has been completed. It was found that the experimental methods of the previous studies could be divided into six categories:

1. in-pile heating in a reactor,
2. slow heating of metal immersed in water or steam,
3. pouring or spraying molten metal into water,
4. molten metal drops falling into water,
5. dispersion of molten metal by an explosive charge, and
6. dispersion of metal by a condenser discharge.

Most of the previous studies were of aluminum and zirconium with some attention given to uranium.

**Aluminum**

The only reports of aluminum reactivity at or slightly above the melting point resulted from in-pile measurements\(^5\) and studies using wires

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heated rapidly by the condenser discharge method. In both cases, only crude estimates of the initial temperature could be made. Experiments using pouring or spraying methods where accurate temperature measurements could be made indicated that no appreciable reaction occurred below about 1200 C. Spraying molten aluminum into water in an "explosion dynamometer" and pouring into water followed by dispersal by an explosive charge showed that violent reactions occurred above about 1200 C. Aluminum at 2070 C gave a stronger explosion in the "explosion dynamometer" than did zirconium at the same temperature. It appears, in general, that the oxide coating is protective at temperatures well above the melting point.

Zirconium

Kinetic studies of the reaction of solid Zircaloy-2 with water and with steam showed that the parabolic law was approximately obeyed at temperatures approaching the melting point. The data for the reaction with 50 psi steam could be represented by

\[ v^2 = 0.1132 \times 10^6 t e^{(34,000 \pm 1440)/RT} \]

8West, J. M., Weills, J. T., Reactor Engineering Division Quarterly Report, June 1, 1950 through August 31, 1950, ANL-4503 (October 1, 1950).
where \( v \) is in units of ml hydrogen per sq cm and \( t \) is in seconds. No evidence was reported in any of the studies of an ignition followed by rapid consumption of the metal such as occurs with most metals in oxygen. All the data including studies by the falling drop method,\(^{15}\) pouring\(^{10,11}\) and spraying\(^{12}\) methods and explosive dispersion methods\(^{13,16}\) are consistent with the idea that rates of molten zirconium-water reactions may be obtained qualitatively by the extrapolation of data obtained with solid samples below the melting point.\(^{16}\) The relatively higher reaction rates obtained by spraying and explosive dispersion methods may be due solely to the greater interfacial area available for reaction.

**Uranium**

The limited quantity of data available on uranium indicates that only surface corrosion occurs at temperatures as high as 1700 C.\(^{12,13}\) Only mild reaction was noted in the "explosion dynamometer."\(^{12}\)

All of the previous studies dealing with molten metal-water reactions have been qualitative in nature. No direct kinetic measurements have been made. It appears difficult to measure true isothermal reaction rates without either self-heating of the sample or cooling due to heat losses to the surroundings. True reaction rates must then be inferred from nonisothermal data. To do this requires detailed knowledge of several important experimental factors:

1. temperature history,
2. reaction surface area,
3. rate of reaction,
4. metal composition,
5. condition of water (steam or liquid) at interface.

Of the available experimental techniques, the condenser discharge method combines a number of desirable features and is under consideration as the principal method of study. None of the previous studies has fully exploited the following desirable features of the condenser method, although the studies were quite helpful: (a) almost instantaneous heating (less than 100 microseconds) to any desired temperature is possible, (b) estimates of the cooling rate may be obtained by a rapid photographic method,\(^{17}\) (c) recent studies have shown that a reproducible particle size distribution may

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be obtained, and (d) measurements of the reaction rates by means of a rapid response pressure transducer appear feasible.

Additional work is under consideration, using inductive heating of a drop or pool of molten metal followed by rapid contact with steam.

Studies will be made of metal-water reactions for aluminum, stainless steel, uranium, and zirconium.

C. Contamination and Decontamination Studies of Boiling Water Loops
(W. B. Seefeldt, S. Vogler)

The fate of a boiling water reactor which has suffered a fuel rupture is only partially known. Continued operation may be possible if (1) gaseous activities can be controlled, and (2) the deposition of solid fission products in the reactor auxiliaries, such as the turbine and condenser, is not excessive. Following such operation, decontamination of the internal surfaces will probably be necessary before again starting the reactor.

To gain an insight into these problems, a boiling loop capable of operation with 50 curies of gamma activity is being designed, with the cooperation of Reactor Engineering Division, for installation in a shielded cell in the Chemical Engineering Building. This loop will simulate operating conditions in a boiling water reactor. A schematic of the loop showing general features is shown in Figure 13. The unit will be constructed of type 304 stainless steel and will be capable of operating at 600 psig. Heat will be

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introduced by resistance heating in the bottom of the left leg. The steam bubbles that form in the left leg lower the average density, causing a natural circulation of fluid: up in the boiling section and riser, and down in the downcomer. The steam is separated at the lower end of the disengaging section, and additional entrained moisture is removed as the steam rises. Irradiated fuel of several types will be inserted where shown. Fission product activities will be introduced into the water by the corrosion of the sample if metal, or by leaching if the sample is an oxide. Some of these activities will be entrained in water droplets in the steam and will be deposited on metal surfaces in the disengaging section containing a sample strip.

The two main objectives of this program are

1. the determination of the magnitude and distribution of the fission product activities deposited on the sample strip. Two important variables are the steam velocity and the sample material.

2. the determination of methods by which these deposited activities can be removed effectively.

The design of the loop is essentially complete and the components are on order.
V. CHEMICAL-METALLURGICAL PROCESSING

Studies to determine the behavior of tracer-level fission elements in the melt-refining process have continued for fuels similar to discharged EBR-II reactor fuel. Results of experiments in which irradiated uranium diluted with "fissium" alloy was melted at 1300 °C indicate that: (a) the fate of iodine may be pressure dependent; (b) at low initial concentration the evolution of xenon takes place by a slow diffusional mechanism; (c) removal of europium may be less complete than for cerium or neodymium; (d) technetium behaves as a typical noble metal, while cadmium is largely removed from the ingot.

The distribution of plutonium and uranium for two melt-refining experiments employing "fissium" alloy containing 69 weight per cent uranium and 20 weight per cent plutonium, and 11 weight per cent "fissium" (see Table 17, page 75, for "fissium" composition) has been followed. Within the experimental error of analysis, the concentration ratios of plutonium and uranium in the charges and ingots remain constant. However, analysis of the skull from a single experiment shows a plutonium enrichment factor of 1.19 relative to the ingot.

A study of the coprecipitation of lanthanum by U₂Zn₁₇ from liquid zinc has been completed. The Doerner-Hoskins coefficient was found to be 0.42 ± 0.05 for all concentrations, cooling, and stirring rates studied, except under conditions leading to high supersaturation. Under the latter conditions, the coefficient is 0.57 ± 0.05. A similar study using ruthenium tracer is in progress.

Auxiliary studies are under way to determine the optimum container materials, method of oxidation prevention, phase separation method, etc., for the utilization of the Pyrozinc processes in large-scale operations. Liquid uranium-zinc alloys have been successfully protected from oxidation by the addition of magnesium to the alloy and the use of a chloride flux (Dow No. 230). The use of a controlled cooling cycle has shown promise as a method of achieving pronounced segregation of U₂Zn₁₇ preliminary to decantation.

Experiments are in progress to determine the decontamination of irradiated uranium possible by the use of the Pyrozinc process. A study has been started to investigate the use of the Pyrozinc process in uranium production.

The electrochemical cell study of the uranium-zinc system has yielded data on the free energy of formation of U₂Zn₁₇. These data have been used to compute the activity and activity coefficients of the uranium in saturated solutions.
Work continues on studies of the thermochemistry of inorganic substances. Construction of an oxygen-bomb calorimeter is nearly complete. A qualitative study of reactions of various substances with fluorine has been started as the first step in the development of the field of fluorine-bomb calorimetry. Design of a high-temperature enthalpy calorimeter is continuing.

Construction of a controlled-atmosphere enclosure for the reaction calorimeters and high-precision measuring instruments has been started. Apparatus has been assembled for the preparation of some calorimetric samples.

In connection with the melt refining of spent EBR-II fuel, the cerium removal data obtained in semi-works runs to date have been correlated as the per cent cerium remaining in the melt versus time at temperature times the ratio of crucible area to charge weight. Emphasis is currently being placed on removal of zirconium from "fissium" melts. The presence of zirconium in high concentrations in "fissium" is not considered beneficial. Removal as the carbide is being further investigated, and the possibility of removal as the boride, nitride or silicide is also being explored.

Work was concluded on the trapping of metals volatilized in the melt-refining process (predominantly, cesium and sodium). "Molecular Sieves" was found to have a high capacity for cesium at 600 and 800 C (30 and 60 weight per cent, respectively), with retention at these temperatures being essentially complete on evacuation to a few millimeters of mercury pressure. Equipment and procedures suitable for plant operation were developed and demonstrated.

In studies on the magnesium extraction of plutonium from uranium, some apparent loss of plutonium from magnesium solutions held in tantalum has occurred. Since tantalum is felt to be a suitable container material, the reasons for this loss are being investigated.

In order to operate well below the boiling point of magnesium, the uranium alloy from which plutonium is extracted is a 5 weight per cent chromium-uranium alloy. The extraction of chromium, although small, results in contamination of the plutonium product. Therefore, the chromium solubility as a function of temperature was measured down to 675 C, where it was very low (about 0.02 weight per cent). Methods of chromium separation based on this low solubility have been postulated, and calculations have been made of chromium build-up in fuel material for various conditions of operation. A possible scheme whereby the chromium problem may be avoided by employing zinc dissolution of the blanket uranium is also presented.
Work on the Pyrozinc Process was continued by measuring the liquid-phase concentrations of "fissium" constituents in zinc and zinc-6 weight per cent magnesium alloys as a function of temperature and cooling rate (see pages 111 and 112). These data indicate the extent of uranium-fission product separation which is possible. Work was also continued on separation of liquid and solid phases, and was started on the recovery of uranium from the uranium-zinc intermetallic compound.

In design and component testing for the EBR-II reprocessing facility several changes have been made in the building design. The air cell of the fuel process building was lengthened to include the disassembly operation. Cooled storage spaces were designed for storage of ingots, slags, or subassemblies. The transfer lock design will be revised. The laboratory and service building has been approved by ANL.

Designs are complete for both types of manipulators, cranes, and their removal device. Tests of electrical brushes in a dry argon atmosphere show a high rate of wear for motor use, but a low rate of wear for feed rail use.

The Junior Cave windows are out for bids. The large window and shutter designs are complete. The effect of intense irradiation upon light transmittance and internal temperatures has been estimated.

A 60-degree circular sector of the argon cell has been mocked up with a prototype window and a circular track for an operating manipulator.

Tests of crucible thermal stability are being made.

Standard 5-gallon containers will be tested for use with dry radioactive wastes. The use of vermiculite for liquid waste is being investigated as is the use of paraffin as a container sealer.

A. Laboratory Studies
   (H. M. Feder)

   1. Melt-Refining Studies
      (N. Chellew, J. Schilb, R. Yonko)

      a. Melt Refining of Short-Cooled Materials

      Additional experiments have been carried out to ascertain the behavior of certain tracer-level fission elements in the melt-refining process. The fission elements investigated during this report period were technetium, cadmium, europium, xenon, bromine, and iodine. The primary purpose of these exploratory studies was to obtain indications of whether or not the element is removed from the purified metal. The quantitative fate
of the element may be dependent on its concentration; these effects will be considered in future studies with material containing higher concentrations of fission products.

For the present experiments, tracer activities were obtained by irradiating normal uranium pins in a thermal flux of about $10^{12}$ neutrons/(sec)(sq cm). The times of irradiation varied from 9 to 98 hours and the lengths of cooling prior to processing from 1.7 to 252 hours. The shortest cooled material was used to follow 2.33-hr bromine-83. The radiation intensity of each pin was measured and several pins having activities around the mean were reserved as controls for each experiment.

The melting furnace and the auxiliary system for sampling the furnace atmosphere were as described in ANL-5820, pages 90 and 91. Provisions were also made for adding small amounts of inactive xenon to the furnace atmosphere and for mixing the gases with a blower. These modifications were tested and shown to aid in obtaining accurate, reproducible samples of the furnace atmosphere in as little as three minutes.

In each experiment, a ten-fold dilution of the irradiated pins with a synthetic alloy was made so that the melt would have a final weight per cent composition of: U, 94.1; Mo, 2.2; Ru, 1.7; Zr, 0.9; Ce, 0.6; Rh, 0.3; Pd, 0.2. Each charge was heated to a nominal temperature of 1300°C and was kept molten for 180 to 190 minutes. Separation of the purified metal was made by top pouring. When information on the effect of pressure on fission product behavior was desired, evacuation of the helium atmosphere in the furnace was carried out during the last third of the melt period.

Table 15 summarizes the distribution of various fission products for three new experiments and includes data from an earlier reported experiment (Run I-36A, ANL-5820, page 92). Comments and further work relating to the behavior of the tracer elements follow:

**Iodine and Bromine**

The halide elements may volatilize from the melt and condense on the furnace walls. Hence, in these runs the furnace was lined with metal foils from which samples could be taken for analysis. A comparison of the iodine remaining in the ingot and volatilized to the furnace walls in experiments conducted with and without pressure reduction (Runs I-36A and I-44A) indicates that the fate of this element may be pressure dependent. The relatively small fraction (about 6 percent) condensed on the furnace walls when melting was carried out without pressure reduction is in rough agreement with results from an earlier (ANL-5730, page 91) experiment carried out at 1250°C, in which less than one per cent of the original activity was volatilized. The high iodine contents of the skulls, about 50 per cent
of the total, and the retention of 40 per cent of the bromine in the ingot are results which need further exploration with higher fission product levels.

**Technetium, Cadmium, Europium**

The results of these experiments indicate that: (a) technetium behaves as a typical noble metal with no selective partition between the ingot and skull; (b) direct volatilisation is the most probable process for the removal of cadmium from the ingot since cadmium compounds are unstable to reaction with uranium under these experimental conditions; (c) europium is drossed out of the melt but the removal is somewhat less complete than for cerium or neodymium.

**Xenon**

Xenon was removed from the poured ingot to the extent of 95 per cent or more. However, the xenon recovered in the ingot, in the skull and in the furnace atmosphere, together, accounted for only a fraction of the total original activity (14 to 30 per cent).

The xenon activity in the furnace atmosphere was sampled during the course of selected experiments. The results for Run I-42A are shown in Figure 14. It may be seen that evolution of the tracer xenon...
became measurable at about 800 °C. This result is not surprising in view of the known rates of diffusion of xenon from solid uranium.\(^\text{19}\) The sample (No. 6) taken about 20 minutes after melting took place, however, showed that only about one-third of the xenon finally evolved was released. These results indicate that at the tested concentration xenon evolution takes place by some surprisingly slow diffusional mechanism. Furthermore, within the limits of the estimated experimental error, reduction of furnace pressure did not cause any noticeable increase in xenon evolution.

To explain the concentration of tracer xenon in the dross fraction and the slowness of its evolution, a hypothesis was set up that its behavior is like that of cesium, another highly volatile fission element. For the latter element it has been suggested that the atoms are trapped at crystal lattice defects of the oxide dross on the metal surfaces (ANL-5255, page 43) and that increasing the initial concentration of cesium decreased the relative fraction so trapped (ANL-5560, page 78). The low recoveries might then be due to loss of some of the trapped xenon on subsequent handling of the dross in air prior to analysis.

As part of a series of tests of this hypothesis two runs were conducted with charges only a twentieth the weight of those previously used, so that the diffusion paths would be correspondingly shorter. The apparatus used in these tests is shown schematically in Figure 15. The

system was designed to permit sampling of evolved radio-xenon when the irradiated material was melted either in vacuum or in helium. An irradiated uranium pin diluted about eightfold with natural uranium was melted and held at a nominal temperature of 1300 °C for three hours. A pin having a radiation intensity similar to that charged was reserved as a control. In the first experiment small volumes (~6 cc) of carrier xenon were added to the previously evacuated furnace tube at 30-minute intervals during the melt period. A Toepler pump was used to maintain a low pressure in the furnace tube and to pump the gases into a sample bulb. The second experiment was conducted in a static helium atmosphere containing one per cent of carrier xenon. Results of these experiments are given in Table 16.

<table>
<thead>
<tr>
<th></th>
<th>Weight (g)</th>
<th>Percentage of Activitya</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vacuum Melt</td>
<td>Helium Atm Meltb</td>
</tr>
<tr>
<td>Uranium Chargec</td>
<td>14.12</td>
<td>16.16</td>
</tr>
<tr>
<td>Crucible</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Button plus Drossd</td>
<td>14.11</td>
<td>16.16</td>
</tr>
<tr>
<td>Evolved</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total Recovery</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Activities determined by the 256-channel gamma-spectrum analyzer.
b) Helium pressure varied from 309 mm at room temperature to 640 mm at 1300 °C.
c) Includes 1.85-gram irradiated normal uranium pin.
d) Maximum button dimensions: diameter, 15 mm; thickness, 6 mm; button and dross (reaction layer) not separated during the experiment.
The fraction of the radio-xenon which was recovered in the furnace atmosphere has risen to 50 to 70 per cent and overall recoveries of 85 per cent were achieved. The evidence therefore appears to support the hypothesis. Additional experiments at higher levels of contained fission gases are planned.

b. Behavior of Plutonium in Melt Refining

Analytical data on the distribution of plutonium and uranium for melt-refining experiments employing an alloy containing approximately 69 weight per cent uranium, 20 weight per cent plutonium and 11 weight per cent "fissium" constituents are reported in Table 17. Procedures followed in these experiments were previously reported in ANL-5759, page 96, and in ANL-5789, page 84. Within the experimental error of analysis (±4 per cent relative), the concentration ratios of plutonium and uranium in the charges and ingots remain essentially constant. In the zirconia crucible run the analysis of the skull is a more sensitive indicator of enrichment, and it showed a plutonium enrichment factor of 1.19 ± 0.08 relative to the ingot.

<table>
<thead>
<tr>
<th>Item</th>
<th>Pressed Zirconia Crucible</th>
<th>Pressed Magnesia Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt (g)</td>
<td>w/o U\textsuperscript{a}</td>
</tr>
<tr>
<td>Charge</td>
<td>353.2</td>
<td>68.8</td>
</tr>
<tr>
<td>Melt Sample Halfway</td>
<td>-</td>
<td>69.0</td>
</tr>
<tr>
<td>through Run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ingot</td>
<td>343.8</td>
<td>68.9</td>
</tr>
<tr>
<td>Skull</td>
<td>9.45</td>
<td>65.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Concentration determined by chemical assay technique; estimated accuracy, ± 4% (relative).
\textsuperscript{b} The refractoriness of this material made its dissolution and analysis subject to unknown errors.

2. Separations by Crystallization from Liquid Metals
(I. Johnson)

a. Coprecipitation

These studies are directed toward understanding the factors which influence the coprecipitation of various metallic elements, present in minor amounts, when a major metallic constituent crystallizes
from a liquid metal solution. A systematic study has been made of the carrying of lanthanum by $U_2Zn_{17}$ crystallizing from zinc. A second study has been started on the carrying of ruthenium.

(1) Lanthanum-Uranium-Zinc System
(M. W. Nathans, K. E. Anderson, I. Johnson)

The carrying of lanthanum has been studied as a function of (a) the lanthanum to uranium ratio, (b) the cooling rate, and (c) the degree of agitation of the melt during the crystallization of the intermetallic uranium-zinc compound. In these experiments a charge of about 300 grams of zinc containing about 1.5 weight per cent uranium and a smaller quantity of radioactive lanthanum was held at 725 to 750 °C in the liquid state, with agitation, for several hours to obtain a homogeneous melt. The charge was allowed to cool. Filtered samples of the liquid were taken during cooling. These samples were analyzed radiochemically for lanthanum and polarographically for uranium. The 40.2-hour La$^{140}$ was used as a tracer in these experiments. The apparatus and technique are described in detail in ANL-5420, page 98. In each case a plot of the logarithm of the number of counts due to the radio-lanthanum against the logarithm of the uranium concentration (as found by analysis of the sample) gives a straight line. Such a quantitative relation is predicted by the Doerner-Hoskins coprecipitation law. It implies that dynamic equilibrium exists at any given instant between the surface of the growing crystal and the solution, and that homogenization of the solid is not attained. It is possible to characterize each experiment by the slope, $\lambda$, of the log-log straight line defined by the equation.

$$\log (La) = \lambda \log (U)$$

where (La) is the fraction of lanthanum remaining in solution and (U) the fraction of the uranium remaining in solution.

When the experimental data are plotted in this manner, one finds that all the points fall on two straight lines. The data are summarized in Table 18.

<table>
<thead>
<tr>
<th>Cooling Rate (C/min)</th>
<th>Stirring During Cooling</th>
<th>(La)/U (Initial)</th>
<th>$\lambda_{obs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Yes</td>
<td>$2.4 \times 10^{-2}$</td>
<td>0.439 $\pm$ 0.019</td>
</tr>
<tr>
<td>17</td>
<td>Yes</td>
<td>$1.7 \times 10^{-4}$</td>
<td>0.462 $\pm$ 0.091</td>
</tr>
<tr>
<td>20</td>
<td>Yes</td>
<td>$9.7 \times 10^{-2}$</td>
<td>0.444 $\pm$ 0.017</td>
</tr>
<tr>
<td>1</td>
<td>Yes</td>
<td>$1.1 \times 10^{-2}$</td>
<td>0.424 $\pm$ 0.010</td>
</tr>
<tr>
<td>7</td>
<td>Yes</td>
<td>$8.5 \times 10^{-4}$</td>
<td>0.494 $\pm$ 0.010</td>
</tr>
<tr>
<td>16</td>
<td>Yes</td>
<td>$1.7 \times 10^{-4}$</td>
<td>0.549 $\pm$ 0.041</td>
</tr>
<tr>
<td>18</td>
<td>Yes</td>
<td>$9.7 \times 10^{-2}$</td>
<td>0.547 $\pm$ 0.028</td>
</tr>
<tr>
<td>20</td>
<td>Yes</td>
<td>$8.3 \times 10^{-4}$</td>
<td>0.561 $\pm$ 0.045</td>
</tr>
<tr>
<td>1</td>
<td>No</td>
<td>$2.6 \times 10^{-2}$</td>
<td>0.462 $\pm$ 0.010</td>
</tr>
<tr>
<td>7</td>
<td>No</td>
<td>$8.5 \times 10^{-4}$</td>
<td>0.494 $\pm$ 0.010</td>
</tr>
<tr>
<td>16</td>
<td>No</td>
<td>$1.7 \times 10^{-4}$</td>
<td>0.549 $\pm$ 0.041</td>
</tr>
<tr>
<td>18</td>
<td>No</td>
<td>$9.7 \times 10^{-2}$</td>
<td>0.547 $\pm$ 0.028</td>
</tr>
<tr>
<td>20</td>
<td>No</td>
<td>$8.3 \times 10^{-4}$</td>
<td>0.561 $\pm$ 0.045</td>
</tr>
</tbody>
</table>
The results show that the coprecipitation of lanthanum is not dependent on the variables tested, except that a significantly greater amount of coprecipitation occurs when fast cooling and no stirring are simultaneously employed. Under these conditions a greater degree of supersaturation is to be expected. Hermann\textsuperscript{20} has discussed the theory and supporting evidence for a diminished selectivity of coprecipitation from supersaturated solutions. An additional low-level (i.e., (La)/(U) = 8.5 x 10^{-5}) experiment, in which the cooling rate was low and stirring was continued during cooling, gave a high value for the coprecipitation constant. This result is believed to be due to loss of the lanthanum by oxidation and has not been entered in the table.

(2) **Ruthenium-Uranium-Zinc System**
(I. Johnson, K. E. Anderson)

Experimental work has been started on the coprecipitation of ruthenium. The experimental method is similar to that used in the lanthanum-uranium-zinc system. Ruthenium will be traced by either Ru\textsuperscript{103} (half-life 39.8 days) formed by neutron irradiation of natural ruthenium or by fission product Ru\textsuperscript{106} (half-life 1 year).

b. **Pyrozinc Process Studies**
(A. E. Martin, C. Wach)

The development of Pyrozinc processes as useful, large-scale operations requires the finding of optimum solutions to many problems. These include container materials, protection of melts from oxidation by additives, fluxes, or unreactive atmospheres, methods for separating liquid and solid phases, etc. Work on some of these problems has generally been qualitative in nature.

**Protection by Fused Salt Fluxes**

The possible use of a fused salt flux as an oxidation barrier necessitated testing of various crucible materials for flux penetration. The flux chosen for testing was Dow No. 230, which contains potassium chloride and magnesium chloride as major constituents and barium chloride and calcium fluoride as minor constituents. Dense grades of porcelain, mullite and pure alumina were impervious. Graphite was highly pervious. Impregnated graphite ("Graphitite") exhibited less, but nevertheless definite, permeability to the flux. Three grades of silicon carbide which differ in the bonding agent are under test. Tests have also been made on the degree of flux protection to various uranium-magnesium-zinc alloys. Weight losses, microstructures and concentrations were followed in each test. The quantitative results will be reported when more experiments have been completed.

\textsuperscript{20} Hermann, J. A., LA-2013 (1957).
Qualitatively, the protection to uranium afforded by the addition of magnesium to the melt and a molten flux cover appears to be good. The ability to handle these melts in air and the absence of a solid dross leads to much simpler operations.

**Protection by Unreactive Atmospheres**

An apparatus has been constructed for studying the protection provided by various gas atmospheres to losses of magnesium and uranium in molten zinc by oxidation and volatilization.

**Separation of Solids**

Some tests were made to determine whether U₂Zn₁₇ can be separated from molten zinc-uranium alloys other than by the conventional hot filtration method. In one group of experiments efforts were made to grow crystals on a cold finger inserted in the melt. The finger was maintained at a temperature lower than the melt but higher than the freezing point of zinc. These experiments were unsuccessful in growing crystals at a rate rapid enough to make this a feasible method.

More successful were experiments which had for their object the segregation of crystals into a limited volume as preliminary to decantation. These experiments will be continued with larger melts under conditions which should lead to more pronounced segregation.

c. **Pyrozinc Processing of Irradiated Materials**
(M. Ader, J. Pavlik)

Apparatus has been set up for studying the decontamination of uranium by the Pyrozinc process. Provisions have been made for using slices of irradiated Oak Ridge slugs and for spiking melts with inert fission product elements to simulate higher burn-up levels. The apparatus was shaken down with several cold runs. One active experiment has been completed and two more are in progress. The results will be reported later.

d. **Pyrozinc Process for Uranium Production**
(A. E. Martin, C. Wach)

Some test work is planned on the reduction of uranium oxides by aluminum to produce a uranium-aluminum alloy as a first step in what might prove to be a cheaper method of producing uranium. Subsequent steps would consist of the solution of the uranium-aluminum alloy in zinc and the separation of uranium from the resulting alloy by crystallization and retorting.

A literature survey has been made and some equipment and material have been procured.
Activities in Zinc Solutions
(I. Johnson, D. Fredrickson)

To obtain data on the free energy of formation of the uranuni-zinc intermetallic compound and on the activities of uranium in zinc solutions electrochemical cells of the form

\[
\text{U(s)} \mid \text{UCl}_3, \text{LiCl-KCl (eutectic)} \mid \text{U (in Zn soln)} \mid \text{W}
\]

have been set up. As reported in the last quarterly report (ANL-5820, page 105) the first cell exhibited extensive polarization. A second cell was set up and operated for several weeks. During operation of this cell it was found that extensive corrosion of the uranium electrode occurred if it was allowed to contact the quartz reaction vessel at the high temperature in the molten lithium chloride-potassium chloride eutectic. Nevertheless, this cell enabled us to determine the approximate emfs as a function of temperature, as well as to study the polarization characteristics of the cell on charge and on discharge. A third cell was set up in which the contact of the uranium electrode with the quartz vessel has been avoided. This cell has given reproducible emf values as a function of temperature.

This third cell contains two independent uranium electrodes in the LiCl-KCl eutectic and one uranium-zinc electrode. The uranium-zinc electrode was initially prepared as 1.02 weight per cent uranium. The lithium chloride-potassium chloride eutectic melt initially contained approximately 7 weight per cent uranium trichloride. The emf-temperature data for the two electrode pairs were found to fit a straight line relation as shown in Figure 16. Note that the change in slope expected at the \(\alpha-\beta\) transition (552°C) is too small to be perceptible. Separate statistical analyses of the two electrode combinations were carried out; they showed that the difference between them was not significant. Consequently, all the data have been pooled to derive the best fit, which is

\[
E = 0.6252 - 5.577 \times 10^{-4} t
\]

where \(t\) is the temperature in degrees centigrade. This equation fits the data with a standard deviation of 0.0003 v. A small correction for the thermoelectric potential developed by the uranium-tungsten leads will be made later.

The results may be used to compute the standard free energy of formation of the uranium-zinc intermetallic compound. This is given by the equation

\[
\Delta F_f^\circ = -53,812 + 38.594 T \text{ cal/g\textsuperscript{atom} of uranium}
\]

where \(T\) is the absolute temperature.
The activity of uranium in saturated zinc solutions may be computed from the equations:

\[ \log a_S = 8.4345 - \frac{11760}{T} \]

This equation for the activity of uranium in zinc may be combined with the equation representing the solubility data as derived from the measurements of J. B. Knighton (ANL-5820, page 126) to obtain the equation for the activity coefficients in the saturated solutions. The best representative equation for Knighton's solubility data is

\[ \log N_S = 4.7760 - \frac{7028.4}{T} \]
where \( N_S \) is the atom fraction of uranium in the zinc solution. Therefore, the activity coefficients, \( \gamma_S \), are given by the equation:

\[
\log \gamma_S = 3.6585 - \frac{4731.6}{T}
\]

3. Problems Related to Chemical Process Steps, Thermodynamics and Physical Data

a. Effusion Experiments
(C. L. Rosen, H. H. Turner, Jr.)

In order to refine the results of the effusion of zinc from zinc-uranium alloys (ANL-5820, page 102) a balance capable of determining weight losses of the effusion cell continuously during a run has been constructed. A schematic representation of this balance is shown in Figure 17. To prevent creeping of the balance beam due to vibrations, the knife edges rest on the inside of Pyrex tubing that has been halved in its length. The weight loss of the sample is counterbalanced by repelling the magnet with the solenoid. The solenoid is calibrated to give the weight in terms of the potential across its leads.

b. Thermochemistry of Inorganic Substances
(W. N. Hubbard)

(1) Chemical Studies
(E. Greenberg, J. Settle)

Combustion and Solution Studies

No non-calorimetric exploratory studies of oxygen bomb reactions have been carried out this quarter. Further studies of this type await the availability of the bomb calorimeter.

Fluorination Studies

A series of studies has commenced in the field of fluorine bomb calorimetry. The development of a fluorine bomb calorimeter would not only make the direct determination of the heats of formation of the elemental fluorides available, but would also be an important adjunct to the study of the refractory materials that are not amenable to oxygen bomb calorimetry. The first phase of this program is the qualitative study of reactions in a fluorine bomb.

Figure 18 is a schematic diagram of the first apparatus used for the fluorination studies. The quartz reaction tube was approximately one inch in diameter and equipped with two internal nickel electrodes and a thermocouple well which are not shown in the diagram.
The general procedure used in the experiments was as follows: A measured length of the metal to be used as fuse wire was connected to the heavy nickel electrodes. A weighed amount of the substance to be fluorinated, contained in a weighed nickel reaction boat, was placed in the quartz reaction tube so that the surface of the sample was from 0.5 to 1.0 centimeter directly beneath the fuse wire. The reaction tube, cold traps and absorption tubes were evacuated, flushed with argon, and evacuated again. Fluorine was admitted to the reaction tube and cold traps to a pressure of approximately 800 mm Hg (absolute).

If the sample ignited spontaneously, the cold trap outlet valve and the fluorine inlet valve were opened to allow fluorine to flow through the reaction tube until all reaction with the sample stopped. If the sample did not ignite spontaneously, the system was allowed to remain
under static conditions for a few minutes to see if any pressure drop occurred, which would be indicative of slow spontaneous reaction. Then the fuse wire was ignited by heating it electrically. The burning wire frequently ignited the sample contained in the nickel reaction boat. After the sample was ignited, fluorine was allowed to flow through the reaction chamber in the same manner as for the experiments in which spontaneous ignition occurred.

At the conclusion of the experiment, the reaction tube, cold traps and absorption tubes were flushed with argon. The nickel reaction boat and its contents, if any, were removed from the apparatus and weighed.

Table 19 is a tabulation of the experimental results of the fluorination studies. Estimates of the completeness of the reaction and qualitative identification of the reaction products were made by visual inspection only, i.e., by noting the amount and colors(s) of the non-volatile products, formation of condensible or non-condensible gases, their colors, etc. Thus, any conclusions expressed are drawn with reservations.

Of the substances tested, boron, niobium, sulfur, selenium, silicon, chromium sulfide, molybdenum disulfide, and zirconium nitride ignited spontaneously in the fluorine atmosphere.

Tantalum, molybdenum monoboride, and titanium nitride exhibited a small amount of spontaneous fluorination, as indicated by an observable pressure drop when the system was under static conditions.
Table 19
RESULTS OF QUALITATIVE FLUORINATION EXPERIMENTS

<table>
<thead>
<tr>
<th>General Observation</th>
<th>Material</th>
<th>Form</th>
<th>Probable Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous Ignition</td>
<td>B</td>
<td>Powder</td>
<td>BF₃</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>Si</td>
<td>Lumps</td>
<td>SiF₄</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>S</td>
<td>Flowers</td>
<td>SF₆ (S₂F₂)</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>Se</td>
<td>Powder</td>
<td>SeF₄</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>Nb</td>
<td>Powder</td>
<td>NbF₃</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>MoS₂</td>
<td>Powder</td>
<td>MoF₆, SF₆ (S₂F₂)</td>
</tr>
<tr>
<td>Spontaneous Ignition</td>
<td>Cr₅</td>
<td>Powder</td>
<td>CrF₃, CrF₄, CrF₅, SF₆ (S₂F₂)</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>ZrN</td>
<td>Powder</td>
<td>ZrF₄, N₂ and/or NF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Mg)</td>
<td>V</td>
<td>Crystals</td>
<td>VF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>Mg</td>
<td>Powder</td>
<td>MgF₂</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Cu)</td>
<td>Al</td>
<td>Dust</td>
<td>AlF₃ (AlF, Al₂F₃)</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Nichrome)</td>
<td>Cu</td>
<td>Powder</td>
<td>CuF, CuF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Nichrome)</td>
<td>CrB</td>
<td>Powder</td>
<td>CrF₃, CrF₄, CrF₅, BF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Nichrome)</td>
<td>CrN₅</td>
<td>Powder</td>
<td>CrF₃, CrF₄, CrF₅, N₂ and/or NF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>W</td>
<td>Powder</td>
<td>WF₄</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Mo)</td>
<td>MoB₉</td>
<td>Powder</td>
<td>MoF₄, BF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>MoSi₂</td>
<td>Powder</td>
<td>MoF₄, SiF₄</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>TiN₉</td>
<td>Powder</td>
<td>TiF₄, N₂ and/or NF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>TiSi₂</td>
<td>Powder</td>
<td>TiF₄, SiF₄</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>ZrB₂</td>
<td>Powder</td>
<td>ZrF₄, BF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Ta)</td>
<td>Ta₉</td>
<td>Powder</td>
<td>TaF₃</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (W)</td>
<td>Teflon</td>
<td>Shavings</td>
<td>C₆F₆ Gases</td>
</tr>
<tr>
<td>Ignited by Fuse Wire (Pt)</td>
<td>Teflon</td>
<td>Wire</td>
<td>PtF₄</td>
</tr>
<tr>
<td>Not Successfully Ignited</td>
<td>Fe, Ni, Sn</td>
<td>Fillings, Wire</td>
<td>Mossy</td>
</tr>
</tbody>
</table>

*Partial spontaneous ignition.

None of the other substances exhibited any observable spontaneous reactions under the conditions of the experiments, i.e., room temperature and approximately one atmosphere pressure of fluorine in the reaction tube.

Tin (40-mesh particle size), iron (40-mesh particle size) and nickel (bundle of 4-mil diameter wire) are the only substances with which ignition has not yet been achieved. However, short lengths of iron (6-mil diameter) and nickel (4-mil diameter) wires connected to the heavy nickel electrodes, and electrically heated, have been ignited.

The substances that ignited spontaneously and continued to burn were completely fluorinated. Most of the substances that required ignition with a fuse wire were less completely fluorinated. It is suspected that the latter substances would have been more completely fluorinated, but for the cooling effect of the nickel boat containing the sample.

In all cases the products were the parent fluorides in their highest fluorination state except as follows: The chromium and copper fluorides obtained were mixtures of different valence states. Aluminum
yielded aluminum trifluoride and a black material of unknown composition, and about 70 per cent of the metal was not fluorinated at all, apparently protected by the black material. The colorless gases from nitrogen or sulfur fluorinations were not further identified beyond being confined to the possibilities listed.

Approximate measurements of the electrical energy used to heat a fuse wire to its ignition temperature in fluorine were made. In each case, the length of wire between the electrodes was approximately 8 cm. The smallest measured amounts of energy in calories were: 5-mil tungsten, 0.8; 4-mil nickel, 1.9; 6-mil iron, 2.2; 10-mil molybdenum, 7.0; 6-mil platinum, 3.5; 8-mil Nichrome, 4.3; 10 x 5-mil magnesium strip, 0.8. The magnesium, molybdenum, and tungsten wires were completely fluorinated, including those portions of the wires which were in contact with the nickel electrodes. The iron, Nichrome, nickel, and platinum wires were completely fluorinated except for that portion in contact with the nickel electrodes.

The results reported above are encouraging enough that a more versatile reaction vessel is being constructed. Further studies will be carried out in the new vessel which will more closely resemble a combustion bomb.

Synthesis and Procurement of Materials

Apparatus has been assembled for the preparation of some carbides and nitrides of uranium and thorium. Experiments with this apparatus are in progress.

A radio-frequency generator for induction heating has been installed in the laboratory.

Samples of seven borides - VB2, WB, W2B, W2B5, TaB, TaB2, and MoB2 - and four carbides - WC, NbC, TaC, and TiC - were received from commercial sources. All of these samples have been analyzed in the spectrochemical laboratory. Except for 0.08 per cent chromium, 0.08 per cent iron and greater than 1 per cent silicon in the VB2 sample, 0.1 per cent iron in the TiC sample and small amounts (several hundredths of 1 per cent) of chromium and silicon in some of the boride samples, all metallic impurities are below the lower limit of detection.

Analyses* by X-ray powder diffraction patterns are still being carried out on these samples in order to determine the solid phases present. Tentative results on three of the boride samples are as follows:

*Performed by D. S. Flukkema, Chemical Engineering Division.
1. TaB. The major phase is orthorhombic TaB.
   \( \text{TaB}_x \ (x = 1.78 \text{ to } 2.00) \) is present as a minor phase. The presence of \( \text{Ta}_2\text{B}_4 \) is also indicated.

2. TaB\(_3\). The major phase is \( \text{TaB}_x \ (x = 2.57) \).
   Further efforts are being made to identify some additional lines.

3. MoB\(_3\)? The major phase is \( \text{Mo}_2\text{B}_3 \). Present as a minor phase is \( \gamma - \text{MoB} \).

(2) Calorimetry
   (R. L. Nuttall, D. Finucane)

   A "controlled atmosphere" enclosure in which the temperature and humidity will be held constant is being built. The walls are now installed and the air-conditioning equipment should be installed in the next quarter. This enclosure will contain calorimeters and critical, high-precision measuring instruments.

Rotating-Bomb Combustion Calorimeter

The rotating bomb combustion calorimeter was received from the shops. After preliminary examination and tests, the calorimeter was returned to the shops for correction of minor defects. The constant-temperature jacket was retained as complete and has been tested for performance.

Illium and platinum-lined bombs are on hand for oxygen combustion calorimetry. A nickel reaction vessel is being built for use in fluorine combustion experiments.

High-Temperature Enthalpy Calorimeter*

Design of the furnace for heating samples to 1500 C has been completed. Basic design of the calorimeter is essentially complete. Detail design is now being done.

A vacuum valve to be installed between the furnace and calorimeter has been designed and detailed drawings are being made.

Some work has been done on a "drop mechanism" for controlling the fall of the sample from the furnace into the calorimeter.

---

*E. D. West, Consultant, National Bureau of Standards.
Auxiliary Apparatus-Temperature Control Equipment

Various types of temperature control equipment are needed in calorimetry. (1) The constant-temperature jacket of the combustion calorimeters will set at a fixed temperature. Its control system consists of a fixed point mercury-in-glass thermoregulator used in conjunction with an electronic relay which operates an intermittent heat source. (2) The constant-temperature bath in which a solution calorimeter may be used will require a control system that can be set to maintain the jacket at various desired temperatures. For this bath a resistance thermometer in a Wheatstone bridge control circuit will be used. (3) The furnace of the high-temperature enthalpy calorimeter will have an isothermal zone in which the sample is suspended. The temperature of the shield surrounding the isothermal core must be carefully controlled. For this system, a thermocouple and a high-precision dc amplifier will drive a recorder and a power control unit which has proportional, rate, and reset action. (4) The adiabatic shield of the high-temperature enthalpy calorimeter into which the sample is dropped must follow the temperature of the calorimeter very closely. For this system a difference thermocouple, dc amplifier, and control circuit, similar to (3) above, will be used. (5) For both the furnace and the calorimeter in the enthalpy-measuring system roughly controlled shields will surround the precision controlled shields. The same type of high-precision control system can be used for these rough shields. However, it may be adequate to build a less expensive photocell amplifier type of system.

The equipment for the control system of the combustion calorimeter has been purchased and given preliminary testing. High-precision dc amplifiers and recorders have been ordered for the control systems of the high-temperature furnace and calorimeter main shields. A photocell amplifier has been built and given preliminary testing for the control system of the guard shields.

c. Studies on Miscellaneous Materials

Tantalum Borides
(C. L. Rosen, H. H. Turner, Jr.)

A sound, clean-looking ingot, weighing approximately 400 g but containing 500 ppm boron, was obtained when molten uranium was contained in a borided tantalum crucible for seven hours at 1250°C in a helium atmosphere. On removal of the uranium, the tantalum boride layer adheres to the uranium below the uranium interface. Microscopic examination shows no signs of any erosion of the boride layer. An unborided, 25-mil wall, crucible was entirely corroded away under identical conditions.

Anodic oxidation of the tantalum has been found to take place when 325-mesh boron is deposited electrophoretically from unstabilized suspensions in methanol, acetone, or isopropyl alcohol. The effect of
the anodization of the tantalum on the corrosion resistance to molten uranium of the fired specimen has not yet been determined.

To obviate the problem of anodization, electrophoretic depositions from organic suspensions of boron using 3 weight per cent zein as a stabilizer have been carried out. Adherent coatings have been obtained on the cathode at potentials as low as 30 v and electrode separations of 1/2 inch. These coatings will be fired in hydrogen at 1200 C to remove the zein, converted to the boride by the usual means (ANL-5422, page 52), and then corrosion tested with molten uranium.

B. Semi-Works Studies of High-Temperature Processes
   (L. Burris, Jr.)

   1. Melt-Refining Studies
      (G. A. Bennett, V. G. Trice, W. N. Thelen, W. H. Spicer)

      The melt-refining process consists simply of melting the fuel in a zirconium oxide crucible, and holding it molten for a period of several hours at a minimum temperature of 1300 C. During this time purification from fission products is primarily effected by: (1) vaporization of the noble gases and other volatile elements such as cesium, and (2) selective oxidation of the highly electropositive elements such as the rare earths and their removal in a surface skin or in a reaction layer which forms along the crucible walls. The noble metals are not removed and are maintained at equilibrium concentration levels* by processing a small side stream of material (called "drag-out") by another process. This side stream will largely consist of the crucible skull remaining after pouring the purified material. Processing of the crucible skull will provide not only for removal of the noble metals, but also for recovery of the fissionable material.

      a. Removal of Fission Products by Melt Refining

      The rare earth elements and yttrium account for nearly 30 weight per cent of the fission elements, and, consequently, their removal is a matter of great importance. For a two per cent burn-up of a "fissium" fuel, the concentration of total rare earth and yttrium elements

      *"Fissium" is the term employed for a uranium fuel containing noble metal fission product alloying agents. The composition generally employed is 3.4 weight per cent molybdenum, 2.6 weight per cent ruthenium, 0.5 weight per cent rhodium, 0.3 weight per cent palladium, 0.10 weight per cent zirconium, 0.01 weight per cent niobium, remainder uranium. This represents the composition of fuel charged to the reactor, i.e., after purification.
in the discharged fuel is about 0.6 weight per cent. Since cerium is the dominant element in this group, it has been used as a stand-in for all the rare earth and yttrium elements. The free energies of formation of the other rare earths and yttrium are virtually identical with that of cerium.

Kinetic data on cerium removal from nine previously reported (ANL-5789, -5820) experiments conducted with "fissium metal" containing ~0.8 weight per cent cerium are plotted in Figure 19. In these runs the "fissium" was liquated in either zirconia or magnesia crucibles at the indicated temperatures for periods up to 5 hours. Cerium concentrations were determined from melt samples taken at various times during the melt period and include all values except two in which analytical difficulties were suspected. Melt stirring of the charge was minimized by the use of a tantalum susceptor. In this figure the per cent cerium retained in the melt is plotted on a log scale against

\[
\text{Time} \times \frac{\text{Crucible Area Contacted}}{\text{Charge Weight}} \quad (\text{min} \times \text{sq cm} \times \text{g}^{-1})
\]

where time is the total melt time. The straight lines representing the data indicate apparent first-order reactions.

**FIGURE 19**
REMOVAL OF CERIUM FROM SYNTHETIC FUEL BY MELTING IN PRESSED MAGNESIA AND ZIRCONIA CRUCIBLES
(Material: 8% fissium; initial Ce conc, ~0.8 w/o)
Data from 9 runs

[Graph showing data points and lines for different crucible areas and temperatures, indicating a trend of cerium retention over time and crucible area contact.]
It is evident that at 1300 °C, cerium removal in magnesia is slower than in zirconia. For melts in zirconia a value of (t A/W) $\sim 1\frac{1}{2}$ times greater is required for equal cerium removal when the temperature is reduced from 1400 to 1300 °C. Data are from experiments in which 1.7 to 3.9 kg of "fissium" was charged to crucibles with diameters between 5.7 and 7.3 cm. Application to largely different A/W ratios should be made with reservation.

Studies of Zirconium Scavenging from "Fissium" Melts

Previous studies by the semi-works and laboratory groups have suggested the possibility of removing zirconium by carbide, boride, silicide or nitride scavenging (ANL-5290, -5388, -5789, -5820). Removals, however, were not high, and for those runs in which poured ingots were obtained (graphite scavenging only) yields were somewhat low. For these reasons, the alternative of not removing zirconium except physically by "drag-out," the method used for the noble metals, was considered. The effect of zirconium in "fissium" in concentrations of 2 to 5 weight per cent is now being investigated by the Metallurgy Division.

Preliminary work by the Metallurgy Division involving zirconium concentrations of around two per cent indicates that its presence may be harmful. The gamma-phase stabilization agents, molybdenum and ruthenium, are removed by precipitation with zirconium at the grain boundaries. This results in conversion to the brittle alpha phase. The radiation behavior is now being determined and is expected to be poor in contrast to that of "fissium" containing little or no zirconium. Because of these factors, methods of zirconium removal are currently being sought.

For a two per cent total atom burn-up ($^{235}\text{U}$ fast fission), 0.23 weight per cent of zirconium would be introduced to the fuel. As yet, there is no knowledge of the zirconium concentration which would be tolerable in "fissium." At equilibrium, however, the total amount of zirconium introduced in the reactor must be removed.

Zirconium Removal as Carbide

Laboratory and preliminary semi-works experiments have shown that under the conditions of interest zirconium carbide is more stable than uranium carbide. The effect of carbide scavenging on ingot yield is not clear from this work. A series of semi-works experiments are currently in progress at one-half plant scale (5 kg) to determine whether carbide scavenging can meet process requirements. Data obtained to date do not permit an evaluation of the efficacy of carbide scavenging for zirconium removal.
Several techniques have been or will be investigated of contacting the melt with carbon. These include the addition of graphite pellets, immersion of graphite rods in the melt, immersion of graphite discs in the melt, graphite coating on the crucible, and the introduction of carbon as uranium monocarbide. Results obtained thus far indicate the desirability of a large contact area.

Tests have been conducted at standard conditions with the liqation for three hours at 1400 C of "fissium" alloys containing 1.0 to 1.5 weight per cent zirconium. X-ray spectral techniques which can detect relative zirconium removals of as little as 0.1 per cent were employed. Removals were determined by the examination of ingot slices.

Treating the melt with graphite pellets achieved a negligible removal of one per cent. The pellets floated on the surface of the melt and were intact at the end of the run. Submerging a graphite rod in the melt resulted in a slightly better removal of three per cent. More important, a 10-mil reaction layer, enriched in zirconium by a factor of three as compared to the melt, formed on the surface of the rod. In both of these runs ingot yields were normal, about 95 per cent.

Increased zirconium removal was realized by using more contact area. A graphite disc, grade 20, 3-inch diameter by 1/8-inch thick, was submerged in the melt. A markedly improved removal of 50 per cent was obtained, but the ingot yield suffered being only 75 per cent. A large reaction mass remained in the crucible after the pour. The graphite disc was no longer intact, but appeared to have been consumed or dispersed through the mass in pieces of various sizes. Examination of the reaction mass showed the principal carbide to be zirconium carbide with lesser amounts of uranium dicarbide (UC₂). The bulk of the mass was apparently "fissium." Examination of the dross layer on the crucible walls showed it to be zirconium-rich relative to the melt by more than 300 per cent. A zirconium-rich layer was noted on the surface of the remaining pieces of graphite.

Previous semi-works attempts to coat zirconia crucibles with graphite were unsatisfactory because the "aqua dag" (graphite dispersed in water) flaked off during the degassing operation. However, in the current series of tests an adherent coating was obtained with Acheson Colloids Company's dag No. 22 (graphite dispersed in aromatic hydrocarbons). Zirconium removal was 29 per cent for this particular charge. Sufficient graphite was present to react with 19 g of zirconium. Ingot yield was the normal 95 per cent. The dross was composed of three separate layers: a shiny black layer not previously observed in melt-refining operations, a layer of bright red crystals rarely observed previously (which may be cerium oxide or carbide), and the usual dull gray slag next to the
crucible wall. The shiny black reaction layer was rich in zirconium as compared to the melt by a factor of 10. Further studies will be made using the graphite-coating technique. An investigation of the use of uranium carbide as a source of carbon will also be investigated.

Zirconium Removal as Compounds Other than Carbide

Because previous work has shown the possibility of removing zirconium as the boride, silicide or nitride, experiments using "fissium" containing 0.5 weight per cent zirconium have been conducted using boron, silicon, and nitrogen as zirconium scavenging agents. Analyses are not yet available.

b. "Fissium" Alloy Irradiated for Melt-Refining Studies

As reported in ANL-5789, page 106, a special irradiation facility was built to provide irradiated specimens for high-activity melt-refining experiments. This is a pressurized water-cooled facility designed for the irradiation of up to 500 grams of 10 per cent enriched uranium at a thermal flux of about $10^{13}$ n/(sq cm)(sec).

A pilot loading of 70 g of natural uranium-"fissium" alloy in 299 g of sodium in a stainless steel autoclave was irradiated for one week. After four days of operation, loss of pressure from the apparatus was observed. Repair of the apparatus is, therefore, necessary and is in progress.

Decanning of the specimen was satisfactorily accomplished in air. After removing the top of the autoclave, the autoclave was immersed in molten paraffin at 120 C. As the sodium melted it collected in a separate phase beneath a protective layer of paraffin. Residual paraffin and sodium were removed from the pin with a kerosene-butyl alcohol mixture.

A second loading of 200 g of 10 per cent enriched uranium-"fissium" alloy has been prepared. It will be irradiated for 100 days to one per cent burn-up.

c. Equipment and Materials Testing

Testing of Freeze-Seal Alloys

As discussed on page 138 of ANL-5820, a low-melting, freeze-seal alloy will be employed to effect a vacuum-tight seal between the bell jar and base plate of the remotely operated melt-refining furnace. A series of tests has been completed to ascertain whether Cerrotru (42 per cent tin, 58 per cent bismuth, mp-140 C) or 40/60 solder (40 per cent tin, 60 per cent lead, mp-183 C) forms a slag under a 5 per cent nitrogen-95 per
cent argon simulated cell atmosphere at 200 C and to determine whether these alloys wet mild steel under these conditions. The equipment for these tests consisted of a gas-tight iron bomb and mild steel crucibles to contain the alloys.

In the first experiment, the alloy samples were placed in the steel crucible within the iron bomb and melted in a resistance furnace. After maintaining the alloys at 200 C for 118 hours, examination showed that neither material had wetted the crucible walls. Therefore, a second experiment was performed in which both alloys were made to wet the crucible walls through the addition of "Fluxine 88" and preliminary melting on a hot plate. These alloys were also maintained at 200 C for a period of 118 hours. The crucible walls were found to still be wetted at the conclusion of this run. Microscopic examination of the sample of both materials from both experiments showed no measurable slag layer.

In order to obtain more definitive information, a dynamic experiment was carried out in which mild steel coupons were dipped in and out of the molten alloys. The time cycle was adjusted so that the coupons were immersed for a period of six minutes and raised for a period of four minutes. Total operating time was 167 hours. As before, the experiment was carried out in a simulated cell atmosphere at 200 C.

Observation after completion of the experiment showed no slag on the surface of the alloys, and no measurable corrosion of the mild steel coupons. The Cerrotru tended to pull away from the steel coupon, whereas the 40/60 solder maintained a tight seal to the coupon (see Figure 20). These results are to be checked in a repeat experiment.

Life Test of Tantalum Susceptor

A life test of a tantalum susceptor, in the presence of, but not touching, a layer of Fiberfrax® insulation is now underway. To date, this susceptor has been maintained for a period of 45 hours at 1400 C without observable deterioration. In this period the susceptor has gone through a series of nine heating and cooling cycles.

Investigation of "Zircoa" Crucible for Melt Refining

The Zirconium Corporation of America manufactures a cast, stabilized zirconia crucible. Several of these were obtained to determine their characteristics. These crucibles are more subject to thermal shock than the Norton dry-pressed crucibles.

* Ceramic fibers composed of 50 per cent alumina and 50 per cent silica manufactured by the Carborundum Co.
2. **Control of Volatile Fission Products**
   (J. Wolkoff)

Until further information is requested by the design group, work was concluded on the development of methods for trapping volatilized but readily condensable materials evolved during a melt-refining operation. The work has been principally aimed at trapping of sodium present on the pins after decladding and the fission element, cesium. The work included the following:

1. Two effective methods were demonstrated for effecting a vapor-tight seal between the crucible and surmounting trap under anticipated conditions of operation.

2. Studies of cesium sorption on surface-active materials were completed. Use of chemical getters was also explored for high-temperature removal of cesium and sodium vapor from an inert carrier gas.
3. Several molten metal solvents (lead, tin, mercury, magnesium, and zinc) were tested for removal of sodium adhering to uranium pins. Wetting of the pins occurred with all except lead, and it, too, began to wet at a sodium concentration of 0.15 weight per cent.

a. Testing of Methods on Equipment for Containment of Volatile Metals
   (A. A. Chilenskas, V. N. Thelen)

Two systems, "static" collection and "gas sweep" collection, were developed and tested for the collection of the sodium and cesium vapors released during a melt-refining operation. For a 10-kg charge, the estimated amounts of sodium (introduced as residual pin coating) and cesium are 44 g and 20 g, respectively. For both systems, a collection capability of greater than 99 per cent of the sodium charged was demonstrated.

"Static" Collection

This method consists of placing a collector on top of the crucible and permitting the vapors to rise and condense on the collecting surfaces and surface-active sorbents such as "Molecular Sieves." The system is illustrated in Figure 21.

![Cone-Type Vapor Collector Diagram]

The apparatus is shown with the gasket loading ring resting on the lip of the crucible. Experiments were also run in which a Fiberfrax gasket was interposed between the loading ring and the crucible.
The experimental procedure followed was to charge about 17 grams of sodium to the steel crucible and about 300 grams of "Molecular Sieves," type 4A-1/8, which had previously been degassed by heating to 600 °C for one hour, to the collector. The lip of the magnesium crucible was ground smooth using a fine-grained silicon-carbide polishing wheel. It was possible to position the induction coil so that the gasket clamp could be heated as well as the crucible.

The vaporization was performed by heating the sodium to about 600 °C under one atmosphere of argon and then rapidly pumping down the system until the vaporization was completed. The start and finish of the sodium boil-up was determined by the change in the slope of the recorded time-temperature curve. The time to evacuate the system from one atmosphere to "boil-up" pressure was about four minutes.

The leakage was determined by water washing the sodium deposit off the Vycor tube surrounding the crucible and collector and titrating the solution with 0.1 N HCl.

Experimental results given in Table 20 show the cone-type collector to give a collection efficiency of better than 99 per cent under proper conditions. The result obtained in Run 50 (16.2 per cent leakage) demonstrated the effect (which had also been previously noted) which occurs when sodium vapor condenses upon the lip of the crucible and gasket. The runs subsequent to Run 50 were performed with the gasket clamp temperature several hundred degrees higher than the vaporization temperature of the sodium, with the resulting increase in efficiency noted in the table.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Sodium Boil-Up (g/min)</th>
<th>Gasket Used</th>
<th>Gasket Clamp Temp (°C)</th>
<th>Sodium Leakage through Juncture (g)</th>
<th>Sodium Leakage (% of charge)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>7</td>
<td>Yes</td>
<td>550</td>
<td>3.6</td>
<td>16.2</td>
<td>Condensation on Gasket and Clamp</td>
</tr>
<tr>
<td>52</td>
<td>8</td>
<td>Yes</td>
<td>800</td>
<td>0.01</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>8</td>
<td>Yes</td>
<td>820</td>
<td>0.01</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>8</td>
<td>No</td>
<td>840</td>
<td>0.12</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>8</td>
<td>No</td>
<td>800</td>
<td>0.17</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

*Estimated by a visual examination of the Vycor tube to be equal to or less than leakage in Run 52. Actual amount deposited was 120 mg (0.7%) through an opening in the gasket clamp which was unknowingly left unplugged.
While an improvement in retention is shown by the use of a "Fiberfrax" gasket, the retention without the use of a gasket, as shown by Runs 54 and 55, is greater than 99 per cent. Although it has not been experimentally verified, the higher retention is believed to be due in part to a gas-sweep through the juncture induced by the sodium acting as the condensable fluid as in a diffusion pump. The heading "Static" Collection had been retained to identify this method with the earlier work reported and to differentiate this system from the system described below.

"Gas-Sweep" Collection

This system employs the use of a forced gas-sweep between the crucible and collector juncture to prevent vapor leakage. The crucible assembly is as depicted for the "Static" system and just the collector is shown in Fig. 22.

FIGURE 22
GAS-SWEEP COLLECTOR

To Vacuum Pump

"Molecular Sieves"

Nichrome Wire Bed Support

Magnesia Crucible

The procedure followed was to place the loaded collector onto the polished lip of the magnesia (no gasket used). The sodium was then vaporized under an essentially constant system pressure while a gas-sweep was maintained through the juncture. The boil-up rate was calculated by determining the beginning and end of the vaporization from the time-temperature curve. The crucible lip was heated inductively as for the "Static" system. Table 21 indicates slight leakage (one per cent) for a gas-sweep rate of 2 liters/min (0.16\(\ell\)/inch of circumference), and no leakage for a gas-sweep rate of 3.5\(\ell\)/min (0.28\(\ell\)/inch of circumference).

Table 21
GAS-SWEEP COLLECTION
(Sodium Boil-Up Rate 2 g/min)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Rate (Liters/min (STP))</th>
<th>Sodium Charged (g)</th>
<th>Sodium Leakage through Juncture (g)</th>
<th>(%) of charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>2</td>
<td>20.9</td>
<td>0.27</td>
<td>1.3</td>
</tr>
<tr>
<td>44</td>
<td>2</td>
<td>21.1</td>
<td>0.06</td>
<td>0.3</td>
</tr>
<tr>
<td>46</td>
<td>3.5</td>
<td>17</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>49</td>
<td>3.5</td>
<td>16.6</td>
<td>-</td>
<td>0.0(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Leakage through the crucible-thermowell juncture occurred when the Sauereisen cement failed. Actual deposit found in tube wash represented 0.4 per cent of the charge.
The Compatibility of Sodium with Various Materials

Both pressed magnesia and zirconia were used in this study. In the early work refractory crucibles were used without the inner steel liner and some penetration of both refractories by the molten sodium was observed. In the case of magnesia, small hairline cracks appeared on the bottom of the crucible along with considerable sodium condensate, whereas in one instance sodium was held molten and then subsequently vaporized from a zirconia crucible without appearing to affect the integrity of the crucible. A small amount of sodium condensate in the bottom of the crucible indicated some penetration.

The attack of molten sodium on Fiberfrax is rapid and deteriorates the gasket whereas short exposures of the gasket to sodium vapor tends to discolor the Fiberfrax slightly without appearing to affect its integrity as a gasket. Similarly, Sauereisen cement No. 1 is rapidly attacked by molten sodium and has only fair resistance to sodium vapor. Applying a wash coating of magnesium zirconate on the dried Sauereisen cement increases the resistance to attack by sodium vapor considerably.

The sorption of sodium as liquid or vapor upon "Molecular Sieves," Type 4A (sodium alumino silicate), discolors the sieves but does not appear to attack the sieves otherwise. The sodium-loaded sieves can be poured from the collector vessels in air without any apparent pyrophoric hazard.

b. Study of Sorbent Materials
(J. Wolkoff, L. F. Dorsey)

Work was concluded at the end of this period on the removal of alkali metal vapor from argon on sorbent beds. This work has application for trapping the volatile metals in the melt-refining process. The general experimental technique and the equipment employed has been reported previously in ANL-5730, page 103. In the concluding work of the last period, the trapping of cesium on activated carbon or "Molecular Sieves," and of sodium or cesium on the chemical getters, aluminum fluoride and iron fluoride, was investigated.

Cesium Sorption on Surface Active Materials

Activated carbon continued to have a high capacity for cesium. At a bed temperature of 800 °C, an average bed loading (weight of cesium absorbed/100 g original bed (dry basis)) of 105.8 weight per cent was measured (Run 50, Table 22), and breakthrough had not yet been reached. The run was terminated when all of the supply cesium had been vaporized. A previously reported loading of 142 weight per cent (ANL-5820, page 120) was obtained at a bed temperature of 583 °C.
Table 22

REMOVAL OF CESIUM VAPOR FROM FLOWING ARGON BY SORPTION

Beds purged with argon at operating temperature before loading with cesium. Argon flow rate 132 ml STP/(min)(sq cm) through beds during vaporization. Gas flows through beds in sequence 4-3-2-1 until breakthrough.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Bed Material</th>
<th>Bed Temp (°C)</th>
<th>Vaporizer Temp (°C)</th>
<th>Position</th>
<th>Initial Wt (g)</th>
<th>Wt Gain</th>
<th>Initial Wt (%)</th>
<th>Per Cent Retention on Evacuation to 2.5 to 5 mm</th>
<th>Per Cent of Cs Load Leachable by Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>Activated carbon</td>
<td>800</td>
<td>572</td>
<td>4</td>
<td>3.73</td>
<td>1.37</td>
<td>114.5</td>
<td>50.8</td>
<td>50.8</td>
</tr>
<tr>
<td></td>
<td>CXA, 0.17-inch pellets</td>
<td></td>
<td></td>
<td>3</td>
<td>3.81</td>
<td>1.61</td>
<td>107.9</td>
<td>54.5</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>3.68</td>
<td>1.86</td>
<td>93.1</td>
<td>50.6</td>
<td>50.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>3.90</td>
<td>1.42</td>
<td>a</td>
<td>54.5</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave</td>
<td>3.78</td>
<td>1.37</td>
<td></td>
<td>50.8</td>
<td>50.8</td>
</tr>
<tr>
<td>51</td>
<td>&quot;Molecular Sieves&quot;</td>
<td>788</td>
<td>560</td>
<td>4</td>
<td>5.70</td>
<td>5.40</td>
<td>39.3</td>
<td>91.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td>4A, 1/8-inch pellets</td>
<td></td>
<td></td>
<td>3</td>
<td>5.59</td>
<td>5.69</td>
<td>29.5</td>
<td>91.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>5.57</td>
<td>5.63</td>
<td>23.7</td>
<td>91.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>5.90</td>
<td>5.63</td>
<td>18.3</td>
<td>91.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave</td>
<td>5.69</td>
<td>5.63</td>
<td></td>
<td>91.7</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>52</td>
<td>&quot;Molecular Sieves&quot;</td>
<td>580</td>
<td>576</td>
<td>4</td>
<td>5.76</td>
<td>6.00</td>
<td>78.5</td>
<td>99.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td>4A, 1/8-inch pellets</td>
<td></td>
<td></td>
<td>3</td>
<td>5.83</td>
<td>5.85</td>
<td>70.5</td>
<td>99.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>5.85</td>
<td>5.85</td>
<td>59.8</td>
<td>99.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>5.90</td>
<td>5.84</td>
<td>34.7</td>
<td>99.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ave</td>
<td>5.84</td>
<td>5.84</td>
<td></td>
<td>99.5</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

Part of bed lost
Run ended before breakthrough

On "Molecular Sieves," average cesium loadings at breakthrough were 27.7 and 60.9 weight per cent for bed temperatures of 800 °C and 580 °C, respectively (Runs 51 and 53, Table 22). These loads are large compared to those of sodium at comparable conditions.

On evacuation to 2.5 to 5 mm pressure at the temperature of sorption, "Molecular Sieves" retained a very high percentage (over 97 per cent) of the sorbed metal (see Table 23). This high retentivity at low pressure contrasts with the data previously obtained for sodium which showed that high retention of sodium occurred only for low loads (5 to 10 weight per cent). It is postulated that cesium is bonded chemically to the adsorber whereas sodium is bonded physically. The bed loadings of cesium versus bed depth before and after evacuation are shown in Figure 23.

The nature of the retention of cesium on "Molecular Sieves" may be affected by the bed temperature. Less than 0.4 per cent of the cesium loaded at 800 °C could be leached with water (Run 51), as contrasted with 55 per cent of that loaded at 580 °C. This effect may be of interest in waste disposal.
Table 23
ALKALI METAL VAPOR REMOVAL FROM ARGON STREAM BY CHEMICAL REACTION

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Metal VapORIZED</th>
<th>Bed Material</th>
<th>Bed Temp (°C)</th>
<th>Vaporizer Temp (°C)</th>
<th>Bed Weights, Dry Basis</th>
<th>Per Cent Retention on Evacuation to 2.4 to 5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>Na</td>
<td>Anhydrous AlF₃, 4/10</td>
<td>649</td>
<td>653</td>
<td>4</td>
<td>9.97 68.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mesh granules</td>
<td></td>
<td></td>
<td>3</td>
<td>9.94 56.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>10.05 15.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>9.76  none</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ave</td>
<td>9.92 33.8%</td>
</tr>
<tr>
<td>55</td>
<td>Na</td>
<td>Anhydrous AlF₃, 4/10</td>
<td>641</td>
<td>654</td>
<td>4</td>
<td>10.66 64.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mesh granules</td>
<td></td>
<td></td>
<td>3</td>
<td>10.64 61.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>10.71 45.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>10.23 29.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ave</td>
<td>10.41 48.2%</td>
</tr>
<tr>
<td>54</td>
<td>Na</td>
<td>Anhydrous FeF₃, 4/10</td>
<td>626 to 647</td>
<td>626 to 644</td>
<td>3</td>
<td>6.79 9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14 mesh foamed vial</td>
<td></td>
<td></td>
<td>2</td>
<td>6.49 6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>6.80 6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ave</td>
<td>6.67 7.5%</td>
</tr>
<tr>
<td>56</td>
<td>Ca</td>
<td>Anhydrous AlF₃, 4/10</td>
<td>574 to 651</td>
<td>564</td>
<td>4 beds</td>
<td>-- (29)%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mesh granules</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>Ca</td>
<td>Anhydrous AlF₃, 4/10</td>
<td>647</td>
<td>655</td>
<td>4 beds</td>
<td>-- (28)%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mesh granules</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Aluminum Co. of America; crushed flaking grade.
†Average for beds 4, 5 and 2.
‡Run ended before breakthrough.
§Run carried beyond breakthrough.

BED DEPTH, inches

**FIGURE 23**

CESIUM SORPTION ON SURFACE-ACTIVE MATERIALS

Beds loaded at 1 atm pressure; evacuation was to a final pressure of 2.5 to 3 mm
Removal of Cesium and Sodium by Replacement Reactions

Additional runs were made to explore the use of clearly defined chemical reactions for alkali metal removal. The reactions tested were

\[
\text{AlF}_3 + 3 \text{Na} \rightarrow 3 \text{NaF} + \text{Al}
\]
\[
\text{FeF}_3 + 3 \text{Na} \rightarrow 3 \text{NaF} + \text{Fe}
\]
\[
\text{AlF}_3 + 3 \text{Cs} \rightarrow 3 \text{CsF} + \text{Al}
\]

Granular beds containing only the salt were employed. For the sodium-aluminum fluoride reaction, the temperature was held below the sodium fluoride-aluminum fluoride eutectic temperature to avoid melting. The runs are summarized in Table 23. In all cases, the desired reaction took place to some extent and reduced metal was observed.

Runs 52 and 55 (Table 23) were made at 650 C to evaluate the sodium-aluminum fluoride reaction. Both were terminated before breakthrough, the resultant average bed loadings being 34 and 49 weight per cent, respectively. These values are higher than obtained previously with the surface-active sorbents under comparable conditions. The reaction appears to be rapid. Some caking and consolidation of the beds occurred at high loadings, tending to constrict the flow of inert carrier gas through them. On evacuation, about 90 per cent of the loaded sodium was retained.

Reaction of sodium with fused grains of iron fluorides was studied in Run 54. A considerably lower average bed loading was obtained (7.5 weight per cent) as compared with the above aluminum fluoride runs. The retention under evacuation was about 80 per cent. The valence state of the iron in the iron fluoride is in doubt at the present.

The cesium-aluminum fluoride reaction was tested in Runs 56 and 57. At a bed temperature of 650 C, melting occurred through formation of cesium fluoride-aluminum fluoride low-melting mixtures. It is not known if the reaction will occur at a temperature low enough to avoid melting.

The work to date has shown that several materials can be employed for alkali trapping. "Molecular Sieves" are most applicable to trapping alkali metals irreversibly to evacuation. It is necessary to keep the sodium load low (less than 10 weight per cent), but this limitation does not exist for the cesium load.
c. **Prior Removal of Sodium by Distillation in Metal Solvent**  
(V. G. Trice, W. H. Spicer)

In the past quarter, tests were conducted to determine the feasibility of a molten metal dip as a means of removing sodium from "fissium" pins. Solvent metals tested were lead, tin, mercury, magnesium, and zinc. Only lead showed promise for removing sodium cleanly. However, sodium concentrations in lead of only 0.15 weight per cent produced wetting. The other metals all wet the "fissium" pins. The approach is not being pursued further.

3. **Magnesium Extraction and Distillation Studies**  
(I. O. Winsch, P. Nelson, R. Paul)

The magnesium extraction process is one in which plutonium is extracted from a molten uranium phase with molten magnesium. Plutonium is subsequently recovered from the magnesium extract by distillation of the magnesium.

a. **Magnesium Extraction**

The plutonium material balances experienced in past extraction runs have raised a question as to reaction of plutonium with crucible materials. Beginning work on this problem was reported in ANL-5820, page 121.

Analytical checks of the magnesium-plutonium extract which was held in a graphite crucible at a temperature of 900 C for a period of eighteen hours have been made. Results indicate that the final plutonium concentration was lower than originally reported in ANL-5820. A revised curve is shown in Figure 24. Based on the final plutonium values, only about 2 per cent of the plutonium originally charged was present in the magnesium ingot after 18 hr at 900 C. Presumably, 98 per cent of the plutonium charged reacted or was absorbed by the graphite. This excessive loss of plutonium in graphite rules out further consideration of graphite as a container material. The use of protective inert coatings on graphite may still be considered.

Several static holding experiments have been conducted in tantalum crucibles. In the first, the Vycor sampling tube broke into the melt and resulted in precipitation of most of the plutonium, presumably as the silicide. The second run was made in three six-hour segments, i.e., over three successive days. The magnesium-plutonium solution was allowed to cool at the end of each day and was reheated to temperature at the beginning of the following day. Samples were taken at the end of each six-hour period. After six hours at 950 C, 100 per cent of the plutonium charged was accounted for in the magnesium phase (Table 24). However,
Table 24

LOSS OF PLUTONIUM FROM PLUTONIUM-MAGNESIUM SOLUTIONS CONTAINED IN TANTALUM AT 950°C

<table>
<thead>
<tr>
<th>Run (^a)</th>
<th>Charge (g)</th>
<th>Weight (g) of:</th>
<th>Per Cent of Initial Plutonium Accounted for in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg</td>
<td>Pu</td>
<td>Poured</td>
</tr>
<tr>
<td>2</td>
<td>460</td>
<td>4.89</td>
<td>422</td>
</tr>
<tr>
<td>3</td>
<td>457</td>
<td>4.81</td>
<td>347</td>
</tr>
</tbody>
</table>

\(a\) In Run 1, the Vycor sampling tube broke and dissolved in melt. Eighty-three per cent of the plutonium was found in heel, probably due to formation of plutonium silicide.

\(b\) Samples are top and bottom portions of grab sample in order given.

\(c\) Samples are from top and bottom of poured ingot in order given.
an unexplainable drop in the plutonium concentration occurred after the first segment as indicated by the 12 and 18-hour samples. The analyses of the dissolved heel and poured ingot samples showed an overall material balance of 91 per cent. The average concentration in the heel is indicated to be two-fold higher than that of poured ingot.

In the third run, the melt was held at 950 C for a period of twenty-four hours. One grab sample was taken at the termination of the run. At best, the plutonium material balance is 87.5 per cent. The fact that the two portions of the grab sample each gave different plutonium values, as did the samples of the poured ingot, may indicate that a heterogeneous rather than a homogeneous melt existed. This could be one explanation for the poor plutonium material balance in this experiment.

The fate of plutonium remains a question. Several modifications of experimental techniques are being considered, one of which will be to employ agitation. The use of a tantalum crucible coated with tantalum monoboride will also be investigated.

An error was made in the calculation of the plutonium distribution coefficients reported in ANL-5789, pages 115 to 118. The plutonium distribution coefficients (mol fraction basis) at 930 C are about 20 per cent higher than reported and are as follows:

<table>
<thead>
<tr>
<th>Successive Simple Batch Extractions In:</th>
<th>Tantalum</th>
<th>MgZrO₃ and Thoria Coated Graphite</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction 1</td>
<td>0.30</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>Extraction 2</td>
<td>0.26</td>
<td>0.22</td>
<td>0.18</td>
</tr>
<tr>
<td>Extraction 3</td>
<td>0.25</td>
<td>0.18</td>
<td>0.22</td>
</tr>
<tr>
<td>Extraction 4</td>
<td>0.29</td>
<td>-</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The values in tantalum are now nearer those previously reported by Nathans and Greenberg in ANL-5730, page 97 (~0.32).

b. Chromium Separation from Plutonium Extract

Most of the experimental work on magnesium extractions has been done with a uranium-5 weight per cent chromium eutectic alloy as the simulated blanket material. The lower melting point of the chromium-uranium eutectic permits an extraction temperature well below the boiling point of magnesium and lessens the problem of container materials. While advantageous because it lowers the melting point, chromium addition to the blanket uranium provides an additional contaminant to the final plutonium product.
It was necessary to obtain more accurate data on the distribution of chromium between magnesium and uranium phases. In order to obtain these data, three extractions were carried out in which about 500 g of magnesium was contacted with 1 kg of uranium-5 weight per cent chromium alloy at 950 C. The melt was agitated with a reciprocating agitator that crossed the phase interface 50 to 100 times per minute. At various time intervals the agitation was stopped and a sample was removed from the magnesium phase.

A graph of the data is shown in Figure 25. The average concentration of chromium in the magnesium phase in contact with uranium-5 weight per cent chromium was 0.156 weight per cent chromium, with a standard deviation of about 0.005 weight per cent. Extraction times in excess of 10 minutes resulted in no detectable change in the chromium concentration in the magnesium phase.

A limited amount of data was also obtained on the solubility of chromium in magnesium extracts at temperatures below the freezing point of the uranium-chromium phase. A magnesium ingot from a previous extraction was re-heated without agitation in an alumina crucible to 900 C and cooled to 675 C. Samples were taken at various times after holding for 30 minutes at 750 C and 675 C. Analytical results shown in Table 25 indicate a considerable amount of chromium precipitation.

The data of Table 25 for chromium concentration in the absence of a uranium phase was compared with the value obtained at 950 C for chromium concentration in the presence of a uranium-5 weight per cent chromium phase on a log C versus 1/T plot. The results indicated that the presence of uranium has little effect on the concentration of chromium in magnesium.

### Table 25

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature (C)</th>
<th>Chromium (w/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>0.082*</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>0.044</td>
</tr>
<tr>
<td>3</td>
<td>675</td>
<td>0.0184</td>
</tr>
</tbody>
</table>

\*The magnesium was separated from solidified uranium-chromium alloy at 800 C after which the magnesium was re-heated to 900 C, and the sample was taken.
The amount of chromium extracted by magnesium at 950 °C, 0.156 weight per cent of the magnesium phase, is 15 to 60 weight per cent of the plutonium that would be extracted, depending upon the relative quantity of magnesium employed for the plutonium extraction. Cooling the magnesium extract to 675 °C would precipitate 88 per cent of the chromium. If the chromium precipitate could be separated, distillation of the magnesium would result in a plutonium concentrate containing two to eight weight per cent chromium. Again, this would depend on the efficiency of the extraction as measured by the amount of magnesium employed.

A further reduction in the chromium content of the plutonium concentrate could be realized if a large percentage of the magnesium were distilled away. Then the remaining plutonium-magnesium concentrate could be removed from the chromium which would have precipitated during distillation. By this method it should be possible to obtain a plutonium product containing less than 0.5 weight per cent chromium.

It has been demonstrated that the chromium transferred to the core material with the plutonium product from the blanket processing would be governed by the following equations:

\[
\frac{(\% \text{Cr}_f)_E}{(\% \text{Cr})_p} = 160 \frac{(\% \text{Cr})_p}{(\% \text{DO})(\% \text{Pu}_p)}
\]  \hspace{1cm} (1)

\[
\frac{(\% \text{Cr}_f)_n}{(\% \text{Cr}_f)_E} = 1 - \frac{(1 - (\% \text{DO})^n}{100}
\]  \hspace{1cm} (2)

where

\begin{align*}
\text{n} &= \text{number of fuel processing cycles} \\
(\% \text{Cr}_f)_E &= \text{weight per cent chromium in the reactor fuel at equilibrium} \\
(\% \text{Cr}_f)_n &= \text{weight per cent chromium in the reconstituted fuel after the nth cycle.} \\
\% \text{Cr}_p &= \text{weight per cent chromium in the plutonium product} \\
\% \text{Pu}_p &= \text{weight per cent plutonium in the plutonium product} \\
\% \text{DO} &= \text{per cent total drag-out of metal in the core processing including losses.}
\end{align*}

These equations are based on 16 per cent burn-up of the plutonium in each cycle (2 per cent total burn-up, 20 per cent fast fission bonus). Table 26 shows the chromium concentration which would build up in the core material for various blanket processes.
Table 26

BUILD-UP OF CHROMIUM IN THE CORE MATERIAL

Basis: 5% metal drag-out including losses.

<table>
<thead>
<tr>
<th>Chromium Removal Process</th>
<th>Magnesium-to-Blanket-Material Weight Ratioa</th>
<th>Cr in Fuel (w/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fuel Processing Cycles</td>
</tr>
<tr>
<td>No chromium removal</td>
<td>1</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Cooling extract to 675 C</td>
<td>1</td>
<td>0.155</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.542</td>
</tr>
<tr>
<td>Partial distillation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and separation from precipitate at 675 C</td>
<td>1</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.054</td>
</tr>
<tr>
<td>90% distillation</td>
<td>1</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.027</td>
</tr>
<tr>
<td>95% distillation</td>
<td>1</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.011</td>
</tr>
<tr>
<td>98% distillation</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

aFor four-stage simple batch extraction, the ratio would be about 3.5.
For efficient counter-current extraction, it would be about 1.

Because of the slow rate of chromium build-up in the fuel, it appears that simply cooling the magnesium extract and removing the chromium precipitate would be adequate for several years of processing. If the increasing chromium concentration proved to be deleterious, the more elaborate partial distillation process could be resorted to.

c. Plutonium Extraction Scheme Using Zinc and Magnesium

Since there is concern over the presence of chromium in the blanket material, it has been suggested that zinc might first be used to dissolve blanket uranium material containing no chromium. After cooling and separating the precipitated U₂Zn₁₇* and the co-precipitated plutonium,

---

*This compound has been previously designated as UZn₉. The formula has recently been reported to be U₂Zn₁₇. See Makarov, A. S., Vinogradov, S. I., Crystallografia, 1, 634 (1956).
sufficient magnesium is added to the uranium-plutonium-zinc concentrate
to make the magnesium-zinc eutectic alloy (54 weight per cent zinc, 46 weight per cent at 500 C - see ANL-5820, page 126), while the plutonium solubility is expected to be high. A schematic flowsheet is shown in Figure 26.

**FIGURE 26**
**FLOWSHEET FOR RECOVERY OF EBR-II BLANKET MATERIAL BY MAGNESIUM-ZINC EXTRACTION AND DISTILLATION**

A small-scale experiment in which 234 g of $U_2Zn_{17}$ was mixed with 160 g of magnesium at a temperature of 800 C for about 3 hours and then allowed to cool slowly gave excellent results. Uranium metal particles agglomerated at the bottom of the ingot, while the main body consisted of the magnesium-zinc eutectic (see Figure 27).

After one or two dummy runs with uranium alone, it is planned to dissolve a uranium-1 weight per cent plutonium alloy in zinc to produce $U_2Zn_{17} + Pu_2Zn_{17}$. The $U_2Zn_{17}$ and $Pu_2Zn_{17}$ will be contacted with the theoretical amount of magnesium required to produce the magnesium-zinc eutectic, and analysis will be made to determine if the plutonium remains in solution and does not precipitate with the uranium.

4. **Uranium Purification by Fractional Crystallization from Liquid Metal Solution**

**Pyrozinc Process**

This is a process by which uranium recovery and purification may be effected by dissolution in zinc at an elevated temperature (700 to 800 C). On cooling, a uranium-zinc intermetallic compound precipitates
FIGURE 27
PHOTOMICROGRAPH OF INGOT FROM MAGNESIUM—
ZINC EXTRACTION
(25 X)

MAGNESIUM—
ZINC EUTECTIC

URANIUM METAL
PARTICLES

DECLASSIFIED
and may be separated from the bulk of the solution, which retains much of
the fission products. The separated uranium-zinc intermetallic compound
may be retorted for separation of the zinc and uranium.

a. Separation of Noble Metals from Uranium by
Pyrozinc Process
(J. B. Knighton, L. F. Dorsey)

In connection with development of the melt-refining process, a small side stream must be processed separately by another process to remove noble metals which are not removed by melt refining. This side stream will probably consist primarily of the crucible skull which must be processed also for recovery of contained fissionable material. The solubility of ruthenium in the presence of "fissium" constituents, all in the concentrations which result on dissolution of "fissium" in zinc, is depressed. The other noble metals remain in solution fairly well as U₂Zn₁₇ is precipitated (see ANL-5789, page 121). Therefore, studies have been concentrated on the separation of ruthenium from uranium.

Use of Fast Cooling to Minimize Ruthenium
Co-precipitation with Uranium

As reported in ANL-5820, page 126, preliminary results showed fast cooling to be beneficial in keeping ruthenium in solution as U₂Zn₁₇ crystallizes. Two fast cooling runs of "fissium" dissolved in zinc have been made in which cooling rates were 33 C/min as contrasted with slow cooling of 0.4 C/min. Only ruthenium and uranium analyses were obtained. The data plotted in Figure 28 show a break in the ruthenium "solubility" curve under conditions of fast cooling. The ruthenium "solubility" data obtained under fast cooling conditions fall very closely, as shown, along the "solubility" curve for ruthenium previously obtained for the ternary system (uranium-ruthenium-zinc) under slow cooling conditions. Although the break in the ruthenium curve seems to have been restored by fast cooling, more data are required to fix the "solubility" curve, particularly the end points.

From the standpoint of achieving uranium-ruthenium separations, it is necessary to operate beneath the flat portion of the curve. Use of an initial ruthenium concentration of 0.01 weight per cent corresponding to a uranium concentration of 0.25 weight per cent) would make possible nearly complete ruthenium separation and 95 per cent recovery of the uranium, which recovery is adequate since only a small side stream is being processed. However, fast cooling imposes additional engineering problems, and process volumes are increased by the use of dilute uranium-zinc solutions.
Similar experiments were carried out using as a solvent a zinc-6 weight per cent magnesium alloy. It has been proposed to use this alloy for skull dissolution (see page 114), the magnesium serving to reduce uranium dioxide present in the skull. It became of interest, therefore, to determine the "solubilities" of the various "fissium" constituents in the zinc-6 weight per cent magnesium system under fast and slow cooling conditions.

"Fissium" with the normal composition shown on page 88 was first dissolved in the zinc-magnesium alloy at 800 °C. Filtered samples were then taken during fast cooling (30°C/min) while the system was mixed. The system was reheated to re-dissolve the constituents and filtered samples were obtained for slow cooling (0.8°C/min) with no mixing.

The data are plotted in Figures 29 and 30. The uranium solubility data are in close agreement for both fast and slow cooling. Palladium remained in solution until a temperature of about 460 °C was reached, when it began to precipitate. The ruthenium behavior is similar to that previously experienced; that is, a break occurred in the "solubility" curve under fast cooling, but was absent in slow cooling. Data were obtained for lower temperatures in the fast cooling run. Concentration changes at 460 °C are the result of MgZn₂ crystallization.
FIGURE 29
LIQUID PHASE CONCENTRATIONS OF URANIUM AND THE NOBLE METALS RUTHENIUM, PALLADIUM, AND MOLYBDENUM IN SOLUTIONS INITIALLY ZINC - 6 w/o MAGNESIUM UPON DISSOLUTION OF FISSIUM ALLOY
(Slow cooling - 50 C/hr without mixing)

FIGURE 30
LIQUID PHASE CONCENTRATIONS OF URANIUM AND THE NOBLE METALS RUTHENIUM, PALLADIUM, AND MOLYBDENUM IN SOLUTIONS INITIALLY ZINC - 6 w/o MAGNESIUM UPON DISSOLUTION OF FISSIUM ALLOY
(Fast cooling - 50 C/min - with mixing)
The molybdenum "solubility" curve for fast cooling is in agreement with that previously reported for slow cooling (ANL-5820, page 126). However, the molybdenum concentrations for slow cooling in this experiment are lower by a factor of three. It is conceivable that, on reheating, molybdenum was not re-dissolved. The subsequent drop in concentration might then be due to a coprecipitation effect.

Separation of Ruthenium from "Fissium" by Zinc Reduction

An experiment was performed to determine if the noble metals can be selectively reduced by zinc from mixtures of uranium dioxide and noble metal oxides with subsequent uranium recovery by magnesium reduction of uranium dioxide in zinc.

A small quantity of EBR-II "fissium" (9.5 grams) was hydrided, dehydrided, and oxidized. Zinc was added and mixed to reduce and take into solution the noble metals. A filtered sample showed that 34.3 per cent of the total ruthenium and 0.4 per cent of the total uranium went into solution at this point. Magnesium was added and after mixing, a filtered sample showed 96.3 per cent of the total ruthenium and 77.1 per cent of the total uranium to be in solution. The temperature of these reactions was 750°C.

These results show the feasibility of selective reduction of noble metals from uranium oxide powder and of uranium recovery by magnesium reduction in zinc solution.

b. Reaction of Uranium-Zinc Solution with Graphite Crucible

Tests have been made to determine if there is any reaction at 750°C between uranium in zinc solution and a graphite crucible. A uranium-zinc solution containing 1.2 weight per cent uranium was placed in a well-degassed graphite crucible and held at 750°C for five hours. Analyses of filtered hourly samples, given in Table 27, showed no significant decrease in uranium concentration. In fact, a slight increase in uranium concentration, which would be due to zinc evaporation, may have occurred.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Uranium Conc (w/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.26</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>1.26</td>
</tr>
<tr>
<td>4</td>
<td>1.26</td>
</tr>
<tr>
<td>5</td>
<td>1.21</td>
</tr>
</tbody>
</table>
c. Dissolution of Skulls from Melt-Refining Operation in Zinc-6 Weight Per Cent Magnesium Alloy

Three runs were made in which 70 to 90 per cent of the uranium in a crucible slag was dissolved in situ in a zinc-6 weight per cent magnesium solution at 800°C (see Table 28). Seventy to ninety per cent of the contained uranium was extracted. The zirconia crucible satisfactorily contained the zinc-magnesium solution.

Table 28

EXTRACTION OF URANIUM CONTAINED IN CRUCIBLE SKULLS BY DISSOLUTION IN ZINC-6 WEIGHT PER CENT MAGNESIUM SOLUTION

<table>
<thead>
<tr>
<th>Total U in Skull (g)</th>
<th>Total U in Zinc-Magnesium Solution (g)</th>
<th>Per Cent U Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.7</td>
<td>61.5</td>
<td>74</td>
</tr>
<tr>
<td>81.4</td>
<td>72.5</td>
<td>89</td>
</tr>
<tr>
<td>102.9</td>
<td>76.5</td>
<td>74</td>
</tr>
</tbody>
</table>

d. Development of Engineering Techniques
   (E. J. Petkus, E. F. Johnston)

Work was continued on the development of equipment and engineering techniques for the Pyrozinc Process (see also laboratory work, pages 77 and 78). Emphasis was placed on the use of filtration for the high-temperature (700 to 800°C) separation of insoluble residues from a molten uranium-zinc alloy, and on the recovery of uranium from a concentrated $U_2Zn_{17}$ phase by distillation.

Filtration Studies

The successful high-temperature filtration reported in the last quarterly (ANL-5820, page 127) was duplicated. Approximately one weight per cent of the charge was left as oxidized material on the filter disc (Grade 40 porous graphite; average pore diameter = 69 microns). However, difficulty continued with zinc vapor condensation in the off-gas system. To overcome this difficulty, a zinc vapor trap was constructed. The vapor trap consisted of a stainless steel pipe cooled on the outside by water-cooled copper tubing. Baffles were inserted in the vapor trap to prevent zinc solid entrainment by the argon gas. The trap worked efficiently as evidenced by the large amount of zinc condensed. The condensed
zinc was melted by turning off the cooling water, and then collected at the bottom of the vapor trap. The necessity of using stainless steel for construction of the vapor trap resulted in rapid corrosion and failure. A graphite-lined or a tungsten or tantalum metal trap would minimize the corrosion problem.

Since both the high-temperature (800 C) and low-temperature (500 C) filtrations have been accomplished and found to be reproducible, no further immediate development work will be done on filtration. Other methods of solid-liquid separation will be investigated during the next quarter.

Recovery of Uranium from $U_2Zn_{17}$

The development of a reproducible method for the volatilization of zinc and coalescence of uranium has been initiated. This is to be a standard method of obtaining a uranium button, free of zinc, which can be analyzed for impurities. The apparatus developed to date is shown in Figure 31. $U_2Zn_{17}$ is retorted in the crucible. The zinc flows up through the baffle and deposits on the graphite cap and stainless steel condenser. The uranium is then coalesced by heating above its melting point.

The stainless steel condenser was originally equipped with copper cooling coils. However, because of the remoteness of the condenser from the crucible, it was found that these were not needed.

Vaporization of zinc under one atmosphere of argon resulted in a moss-like type of condensate. Operation under vacuum, however, resulted in a bright metallic deposit of zinc. The solid zinc condensate was easily removed by peeling from the stainless steel and graphite surfaces.
Although the zinc has been successfully volatilized, complete coalescence of the uranium has not yet been achieved in the quantities employed (about 100 g). On heating to 1200 C, the uranium was partially coalesced into buttons and partially into a sponge-like mass. The sponge-like mass was not pyrophoric. In the future, larger quantities of uranium will be used in an attempt to achieve complete coalescence of the uranium.

C. Fuel Processing Facilities for EBR-II
(J. H. Schraidt)

1. Process Auxilaries and Building
(G. J. Bernstein, J. Graae)

Previous quarterly reports (ANL-5789 and ANL-5820) contain general descriptions of the EBR-II process plants. To simplify construction of the reactor building it was decided to move the spent fuel disassembly operation to the Fuel Process Building. To accommodate the necessary equipment for this operation the inside length dimension of the air cell was increased from 33 feet to 47 feet. This extension can be made without increasing the size of the Process Building and with very little structural change.

Storage spaces in the air cell for fuel subassemblies, and in the argon cell for ingots and slags, are presently under design. Approximately fifteen storage pits made of 10-foot lengths of 12-inch diameter pipe will be provided in each cell. These pipes are being provided with external cooling coils to remove fission heat generated in the stored materials.

The architect-engineer has submitted preliminary designs for the transfer lock mechanism. The lower lifting mechanism is in the form of a crane trolley which travels between the opening in the air cell floor and the lock. This design is being revised. Additional drawings of first floor layout and building ventilation have been received and are being reviewed.

a. Manipulators and Cranes
(J. Graae, G. J. Bernstein)

Layout and assembly drawings of the General Mills operating manipulator were approved and detailed shop drawings are being made. Specifications and layout drawings for the cell cranes are complete and bids are being invited. The trolley and manipulator removal device has been detailed and will be built for installation and testing in the mock-up area.
b. Material Testing  
(G. J. Bernstein, L. F. Coleman)

Tests of electrical brushes in dry argon atmosphere have continued. The tests on the Howard Industries 1/10-hp motor have shown a high rate of brush wear (approximately 2 mils/hr) with a variety of "high-altitude" brushes. Similar motors operating in air on a test manipulator showed little wear. This problem is still under study.

Dry argon atmosphere running tests have started on an EEMCO motor (Type C743C, 1/4 hp) to determine brush wear. These motors are presently specified for use in the General Mills operating manipulator.

Slip rings tests of a variety of "high-altitude" brushes running on metallic rings in a dry argon atmosphere showed essentially no wear (0 to 4 mils total) after more than 80 hours of operation. Therefore no problem in slip ring or feed rail power pickup design is anticipated in the argon cell.

A number of elastomers and refractory materials are being irradiated in the irradiation facility to determine potential merit as gasket or insulating materials.

c. Shielding Windows and Optical Viewing Devices  
(T. W. Eckels, J. Graae)

The shielding window design has been completed. Detailed drawings have been made of the steel cavity liner in which the windows will be installed, as well as of the two inner removable glass slabs and a sealing glass panel. Construction specifications have been drafted and will be submitted to prospective manufacturers. The viewing angles for the shielding windows are shown in Figure 32.

Steel shutters for protection of the radioactive side of the windows have been designed. They will be driven by electric motors. All parts, shutters, motors and drive can be replaced remotely.
The stereo-optical viewer has been completed and performs its function of giving improved depth perception when viewing operations through the five-foot window in the cell mock-up area.

The wide angle peephole "periscope" under contract with Pacific Optical Co. is due to be shipped by the end of March. A location is being prepared for it in the new cell mock-up. Specifications have been completed for a wall periscope for the same area. This "L"-shaped instrument is to be installed through an ANL Model 8 manipulator wall tube at a height of ten feet above the floor.

The specifications for the six Laboratory and Service Building junior cave shielding windows have been completed and bid invitations sent out.

**Shielding Window Radiation Damage**

*(L. F. Coleman, T. W. Eckels)*

A method has been devised to calculate the temperature profile at equilibrium in a shielding window exposed to intense gamma-radiation fields (10^6 r/hr). Several typical cases have been calculated, assuming a monochromatic source (1.5 Mev) and also for a typical EBR-II spectrum source. This method differs from previously published methods in that corrections for ambient conditions are applied and finite glass thicknesses are used. The accompanying table gives the results of three calculations by this method for a 10-kg EBR-II source at varying distances from the window.

<table>
<thead>
<tr>
<th>Source Distance (feet)</th>
<th>Depth of Maximum Temperature (feet)</th>
<th>Maximum Temperature (F)</th>
<th>Front Face Temperature (F)</th>
<th>Maximum Temperature Gradient (F/ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>0.24</td>
<td>144</td>
<td>140</td>
<td>58</td>
</tr>
<tr>
<td>1.0</td>
<td>0.40</td>
<td>280</td>
<td>230</td>
<td>490</td>
</tr>
<tr>
<td>0.36</td>
<td>0.45</td>
<td>1200</td>
<td>680</td>
<td>4600</td>
</tr>
</tbody>
</table>

These results are of a preliminary nature, but it is felt that proposed refinements in the calculation method will cause no great change in the results. Several meetings have been held with engineers from two shielding window manufacturers in an attempt to determine the effect of such temperatures and gradients. Although no simple stress analysis seems possible, it is probable that a 10-kg source will cause failure in a thick plate if it is closer than one foot for a sufficient period of time. Various mechanical methods of minimizing this effect have been considered, but limiting the period of close proximity by administrative control seems at present the most practical approach. The permissible period must be determined by studies of transient conditions for typical cases.
A study of transient temperature conditions covering a ten-hour period was made utilizing the method of finite differences. Fifteen-minute intervals were used for the first two hours, while one-hour intervals were used for the succeeding eight hours. Another study for one very restrictive set of transient conditions was made with a simple electrical analog. Additional studies will be made using a modified electrical analog. Results to date are only of a preliminary nature and therefore will be reported later when refinements have been made in the calculations and analog.

Preliminary curves have been made of internal light transmittance as a function of both cerium oxide content and integrated gamma flux for 2.7 and 3.3 density shielding glasses. The transmittance data upon which these curves are based were furnished by Remote Control Division, which has been making irradiation studies on samples of special formula glasses.

Evaluations of a number of different glass combinations in one basic window design similar to the window described in ANL-5820, page 134, have been made in an attempt to find the optimum combination to avoid permanent damage to the oil-filled assembly and to retain the best initial transmittance. It appears from these studies that a shielding window made of 3.3-density glass for all the major pieces should give the best over-all service. The four parts of the window progressing from the observer side inward are: (1) an oil-laminated section slightly over forty inches thick, (2) a glass plate about two inches thick which will be gasketed to make a gas-tight seal for the argon atmosphere, (3) a semi-fixed block about nine inches thick, and (4) a readily removable block about ten inches thick. It was originally planned to use 2.7-density glass for the semi-fixed and removable pieces, but a reasonable thickness will not properly shield the oil-laminated section. Also, from the analysis, 2.7-density glass in this location would give less initial transmittance and also less a; the high integrated doses expected. It has been estimated on the basis of present information that 3.3-density glass containing one per cent cerium should be used for the first 34 inches from the observer's side, with the balance of the window made of normal production 3.3-density glass containing approximately 1.75 per cent cerium. These figures could be subject to modification as further data become available.

d. Cell Gas Purification - Oxygen Removal
(L. F. Coleman)

The cell gas treatment mock-up facility was run throughout this period to test the components further and to furnish gas for motor and spark breakdown testing. The composition of the gas was approximately 10 ppm oxygen, 5 per cent nitrogen and 95 per cent argon at equilibrium.
Breakthrough occurred in the dryer ("Molecular Sieves") at about 20 per cent of the anticipated loading. A check on recent literature published by the dryer manufacturer indicated that the reasons for the breakthrough were twofold: regeneration had not been done under ideal conditions, and the capacity of the "Molecular Sieves" is low at the oxygen concentrations of the test. At an oxygen level of 1000 ppm the dryer capacity for the resultant water is 17 pounds of water per 100 pounds of dry absorbent. At 100 ppm it is 9 pounds and at 10 ppm it is 4 pounds.

The operational capacity of the full-scale Process Plant unit can be improved over the mock-up system in several ways. Type 5A rather than type 4A "Molecular Sieves" shall be used. Regeneration shall be with very dry air even if a separate pre-dryer is necessary; it shall be accomplished at a temperature in excess of 480 F. The efficiency of the blower after-cooler system shall be increased to permit operating the dryer at less than 80 F.

e. **Cell Lighting**

*(L. F. Coleman, T. W. Eckels)*

The shielding windows in the cell will reduce the light intensity by a factor of approximately 20. Such attenuation makes imperative an efficient lighting system. One possible system furnishes about 100 foot-candles as basic lighting from eight overhead 3-kw mercury vapor lamps and intensities up to 5000 foot-candles from local lights; representative illumination tests have shown this to be a desirable range of levels. Two problems with this system are changing the overhead lamps and high starting voltage, which might result in arcing.

Wooden models were used to test two concepts of replacing tubular-shaped lamps installed on the cell ceiling. Both were tested in the cell mock-up and then retested after revision. One concept was rejected as unworkable; the other will be retested after further modifications.

The starting voltage of the tubular 3-kw mercury lamps is 850 volts rms with a 1200-volt peak, which is sufficiently above the minimum sparking voltage to warrant further work. Sparking tests have been run in air, 95 per cent argon and 5 per cent nitrogen, and 100 per cent argon. The tests show discrepancies but indicate that gaps less than 0.05 inch and radii less than 0.03 inch should be avoided.

A lamp fixture for a 400-watt mercury bulb of the General Electric E-1 shape and size is being fabricated for the Chemical Engineering Division hot chemistry cave. It will be tried for manipulator operations.

*A product of Linde Air Products Co.*
in the cell mock-up as soon as it and the mock-up are completed. Weight of the removable part is being held to a minimum. The fixture is designed to be replaced remotely and has its own male electrical plug. The single fixture is designed to install in either the vertical or horizontal position.

2. **EBR-II Fuel Processing Mock-Up Facility**  
   (D. C. Hampson, T. F. Cannon)

   A full-scale sector of the proposed process plant has been mocked-up. The circular tracked, prototype operating manipulator will be used in this area. Work is continuing to improve the melt-refining furnace and auxiliary equipment.

   a. **Argon Cell Mock-Up**  
      (D. C. Hampson)

   A sector (approx 60°) of the argon cell has been mocked-up (see Figure 33). This is a full-scale section of the working area of the cell. The outer wall is five feet thick and contains the existing prototype five-foot thick, all-glass shielding window (see ANL-5820, page 134, Figure 58) in the center section. This window has an included viewing angle of 94°. The other two sections are not equipped with windows, although the plant cell will contain window apertures in this wall. The inner (central control area) wall is in three sections. The center section contains a window opening covered by Plexiglas plates. This opening is framed to give the same viewing angles (110°) that will be obtained with the proposed shielding windows. In order to obtain the proper viewing area without the diffraction advantage of an all-glass unit, it was necessary to taper the window outwards to the cold face of the cell wall. This is the opposite taper that exists in the actual window. Replaceable framing allows the center line of this window opening to be moved upwards or downwards. This movement is required because the level of the floor in the plant central control area will be three feet lower than the cell floor. In the mock-up facility these two floor heights are the same. By changing the window framing the center line of the window can be shifted to conform to the proper height from the cell floor or from the central control area floor.

   Provisions are being made in this wall to install the inner or hot-face pane of glass. The frame for this pane of glass is hinged and will be rotated into the cell for removal with the crane and manipulator. Provision for ready removal is necessary since this pane will suffer the most rapid radiation damage.

   This inner wall was made approximately three feet thick to match visually the apparent thickness of the five-foot thick, all-glass shielding window. The distance between inside faces of these two walls
is sixteen feet. A transite skin is being placed on the inside, or hot, faces of these walls and a plywood skin on the outside, or cold, faces of these walls. The manipulators can be controlled from either the inner or the outer cold face of the cell. The area enclosed by the inner wall represents a segment of the central control area.

A track has been installed to support the prototype operating manipulator. This manipulator will pivot at a point above the central control area and run on the circular track located at the hot face of the outer wall.

The track for the existing articulate General Mills manipulator has been relocated so that this manipulator will be able to serve most of the circular mock-up area.
In addition to testing the prototype manipulator and the equipment in a circular grid, this facility will be used to test and develop the cell service facilities. This includes lighting, and handling of lighting fixtures, position of equipment locaters and holddowns, service slots and service connectors.

b. Melt-Refining Furnace and Base Plate Freeze Seal

A new base plate and bell jar have been built. Leak tests of the freeze seal, which joins the bell jar to the base plate, were made. At the time of these tests the only openings to the base plate were the vacuum and vacuum gauge lines. There were no openings in the bell jar. The tests were made by repeatedly melting the seal, lifting the bell jar and allowing it to air cool for five minutes and then replacing it in the molten solder. After the solder had solidified the leak rate was determined at about 40 microns pressure. The leak rate of $0.007 \pm 0.001$ cubic inch free air per minute is equivalent to a pressure rise of about 12 microns per hour or to a leak rate of 100 micron-liters per minute. The seal alloy used was 58 per cent Bi-42 per cent Sn.

At the completion of these tests the bell jar was returned to the shop for addition of holes for power leads, windows, tilting rod, etc. The furnace should be back in operation early in the next quarter.

The stabilized zirconium oxide crucibles procured for the prototype melt-refining furnace appear to be quite sensitive to thermal shock. The crucibles are $6\frac{3}{8}$-inch OD by $9\frac{1}{8}$-inch high by $5/8$-inch wall. In the degassing process and in uranium-melting operations cracks developed during the heating period. The crucibles were heated to 1300 C under vacuum at a rate of 7.3 C/min during degassing and to 1300 C in inert gas at a rate of 8.7 C/min during uranium melting. In all cases, under these conditions the crucibles developed cracks. A test was made on a new crucible which was degassed at a heating rate of 4.5 C/min to 1200 C and then cooled at 5 C/min; only a few hairline cracks developed. The crucible was then heated at the normal run rate (8.7 C/min) to 1300 C; no new cracks appeared. Additional tests will be made to establish crucible stability.

c. Manipulator Operations

The tendency for the manipulator telescopic tubes to stick (see ANL-5820, page 139) was determined to have been caused by a bent tube. This tube was replaced, but the difficulty was not completely eliminated. General Mills, Inc. is testing a new type of bearing support for the telescopic tubes. Results of these tests should be available in the next quarter. At this time a decision will be made concerning the solution of this problem.
3. **Process Cell Solid Wastes**  
(P. Fineman, G. J. Bernstein)

Samples of standard 5-gallon steel containers have been received from one manufacturer. These containers have crimped cover seals and have been closed using standard equipment but no gaskets. They will be tested for leak tightness to determine their suitability as possible containers for dry highly-radioactive wastes.

A preliminary design for a disposable high-efficiency filter in a vacuum-tight case has been made. This filter will be used in conjunction with the melt-refining furnace to protect the vacuum pump from particulate activity.

4. **Laboratory and Service Building**  
(P. Fineman)

The drawings and specifications for this building are now complete and have been approved for construction by ANL. A bid package which included this building was sent on April 1, 1958 to the Idaho Operations Office. Construction bids will be invited by the Idaho Operations Office.

Several items of equipment, related to the Junior Caves and hot waste disposal operations, were not included in this bid package. Their design, fabrication, or purchase is being initiated by the Chemical Engineering Division. These items include:

1. Model 8 manipulators and manipulator installation handler
2. Shielding windows
3. Sample-transfer shield
4. Transfer shield for pipe field storage
5. Hot-waste disposal equipment and shield
6. Fume hood and trays for Junior Cave.

5. **Liquid Waste Treatment**  
(P. Fineman, W. A. Rodger)

The use of expanded vermiculite (Zonclite Company, Chicago, Illinois) appears to offer a simple method for stabilizing contaminated liquid wastes, particularly the high-level activity solutions from the Junior Caves. The absorptive quality of the vermiculite would be utilized in this technique.

To demonstrate the feasibility of this approach, bench-scale experiments were conducted with simulated non-radioactive acidic and neutralized waste solutions. The solutions were added, without mixing, directly to the vermiculite. This was done to simulate the simplest of plant operating conditions. The method proved to be quite satisfactory. When the
liquid addition rate was too rapid, any free liquid not initially absorbed was absorbed within 10 to 15 hours. The acidic wastes appeared to absorb better than the neutralized ones and were absorbed satisfactorily up to 60 per cent of the theoretical capacity of vermiculite (grade No. 3: 4 gal retained water/cu ft). At this point, the vermiculite was observed to be still free flowing and did not release liquid unless compressed.

Experimentation is being continued to determine the maximum absorptive capacity for this material. A test will be made to determine if there is any pressure build-up (gas release) when contacting the vermiculite with acid solutions.

Paraffin was tested as a possible material for sealing containers employed in waste-treatment operations. In the vermiculite experiments, the paraffin was melted and added in two steps, allowing the paraffin to harden between the two additions. The first layer served as a "prime coat" for the subsequent addition and reduced the amount of paraffin needed to effect the seal. This method appears to be a practical and inexpensive way of sealing containers. Wax may be substituted for the paraffin if a higher melting point material is needed. Radiation stability remains to be investigated.
VI. ANALYTICAL RESEARCH AND SERVICES

A. Analytical Service and Development
(R. P. Larsen)

A method has been devised for the determination of 0.001 per cent sulfate in uranium trioxide. Sulfur trioxide liberated on ignition with vanadium pentoxide is reduced over hot copper to sulfur dioxide, which is absorbed and determined spectrophotometrically.

The selective dissolution of uranium from LMFR samples has been accomplished by first amalgamating the bismuth and then leaching the uranium with 4 M hydrochloric acid-1 M hydrofluoric acid. It is expected that a similar procedure can be used for magnesium and zirconium.

1. The Determination of 0.001 Per Cent Sulfate in Uranium Trioxide
(R. P. Larsen, L. E. Ross, N. Ingber)

A method has been devised for the determination of 0.001 per cent sulfur in uranium trioxide. By mixing the oxide with vanadium pentoxide and igniting in a quartz furnace tube at 1000°C, quantitative volatilization of the sulfur as trioxide is attained. The trioxide is reduced to dioxide with hot copper and the dioxide absorbed in a dilute solution of sodium tetra-chloromercurate (Figure 34). The nitrogen which is used as the carrier gas is given a precautionary prescrub with the same reagent. The colored compound formed when the mercuric sulfate complex reacts with p-rosanaline hydrochloride and formaldehyde permits the determination of 10 ± 1 micrograms of sulfur. Pre-ignition of the vanadium pentoxide, the quartz boat, and the furnace reduces the blank to less than 2 micrograms of sulfur. If the sample contains less than one per cent nitrate, the nitrogen oxides are satisfactorily reduced by the copper. Samples having a higher nitrate concentration are pre-ignited at 600°C to reduce their nitrate content to an acceptable level.

2. The Selective Solution of Uranium from Bismuth Alloys
   (R. J. Meyer, E. King)

A method has been developed for the selective solution of uranium from bismuth alloys. By amalgamating the sample and then leaching the amalgam with a 4 M hydrochloric-1 M hydrofluoric acid mixture, all the uranium and only 0.1 per cent of the bismuth are brought into aqueous solution. Because the separation of a minor constituent from the major one in an analytical procedure is almost always more rapid and dependable and leads to much smaller solution volumes, the amalgam-leach separation should be superior to the sulfide precipitation,\textsuperscript{23} anionic absorption\textsuperscript{24} and bromide distillations\textsuperscript{25} of bismuth now being used at other laboratories. It is expected that the method can be extended to other minor constituents of the alloy such as zirconium and magnesium.

Dilute hydrochloric acid and dilute sulfuric acid were first tested as possible leach solutions for the bismuth amalgam, but neither gave complete uranium recovery. Progressively lower recoveries of uranium with hydrochloric acid on successive tests indicated that uranium was probably being slowly oxidized in the ground alloy then being used. By adding fluoride to the leach solution, all the uranium was satisfactorily solubilized.

The amalgam-leach method has been checked by comparing the results obtained on two alloys with those obtained by another method. A sample prepared at Argonne and assayed polarographically was found to contain 273 ppm when the amalgam-leach separation was used and 269 ppm when the bismuth sulfide precipitation was used. A sample supplied by Brookhaven National Laboratory was analyzed polarographically and spectrophotometrically after an amalgam-leach separation. The values of 815 and 850 ppm which were obtained compare very favorably with the Brookhaven value of 830.

Approximately 0.1 per cent of the bismuth is dissolved by this leaching procedure. While this quantity of bismuth will not interfere with either the polarographic or dibenzoyl methane spectrophotometric uranium determinations, it cannot be tolerated in the spectrophotometric determination of zirconium with alizarin. Similar interferences are to be expected in any magnesium determination. The bismuth content in the leach solution can be reduced by a factor of 100 by adding zinc metal to the leach solution before separating it from the amalgam. Copper, which interferes

\textsuperscript{24}Milner, G. W. C. and Edwards, J. W., A.E.R.E. C/R 2143
\textsuperscript{25}Milner, G. W. C. and Barnett, G. A., A.E.R.E. C/R 2146

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in the polarographic determination of uranium, is also effectively removed. Zinc will not interfere in either alizarin method for zirconium or in the polarographic determination of uranium.

The procedure presently used for the determination of uranium in bismuth is outlined below. A one-gram sample of alloy is stirred with approximately 10 ml of mercury and exactly 10 ml of a 4 M hydrochloric-1 M hydrofluoric acid mixture for twenty minutes. Approximately 0.1 gram of granulated zinc is added and stirring is continued for an additional ten minutes. An aliquot of the aqueous solution is evaporated to dryness after the addition of nitric acid to oxidize the uranium. The residue is taken up in 2 M sodium acetate-0.1 M EDTA* solution and diluted to volume. Uranium is determined polarographically on this solution using the standard addition technique.

B. X-Ray Spectrochemical Analysis for Molybdenum and Ruthenium in Uranium-"Fissium" Alloys
(D. S. Flikkema, R. V. Schablaske)

To define the inter-element effects in the X-ray spectrochemical analysis26 for molybdenum and ruthenium, (ANL-5633, pages 141 to 146) and to extend its usefulness, additional work has been carried out. Additional alloys, designated FST in the tables, were prepared from master "fissium" alloy, pre-melted high-purity uranium, Fansteel molybdenum wire and American Platinum Works ruthenium powder. The melts were made in bottom-pour thoria crucibles by means of a high-vacuum induction-heated furnace. After ten minutes at 1500 C the melts were poured into a graphite mold surrounded by a water-cooled copper block. The resulting ingots, which were one inch in diameter and about one inch in length, were lathe-trimmed to squat cylinders.

The homogeneity and the composition of each alloy were determined by X-ray spectrometry in conjunction with chemical analysis. Thin slices for chemical analysis were taken on both sides of a thicker middle section, whose faces then were polished metallographically for examination in the spectrograph (ANL-5633, page 137). If the emission line intensities from masked regions of each side showed the section to be homogeneous lengthwise and in the face plane, the thin slices were analyzed chemically to establish their composition. Otherwise, the pieces were arc-melted and re-examined. The chemical method used for ruthenium involved separation of the ruthenium by distillation of its volatile tetroxide and subsequent spectrophotometric (absorption) determination as hexavalent ruthenate.

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*Ethylene diamine tetracetic acid

26 Proceedings of the Sixth Annual Denver Research Institute Conference on X-Ray Analysis, pages 387 to 398 (1957)
Molybdenum was separated from the uranium and other interferences by solvent extraction with butyl acetate and was determined by the thiocyanate spectrophotometric method.

Previously it had been found that at between 1.5 and 5 weight per cent molybdenum the working relation, molybdenum Kα X-ray intensity versus molybdenum concentration, could be established well enough for a relative reliability of ±2 per cent with only two well-standardized alloys near the extremes of the range and without correcting the intensities in any way other than subtracting background. To reduce this error towards the limit imposed by the summed effects of counting, instrument and chemical analytical errors in calibration, it was necessary to correct for the effect of variable ruthenium content on molybdenum Kα X-ray intensity. Corrections calculated from available mass absorption coefficients were checked by empirical determinations at three levels of molybdenum concentration, 2.4, 5.7 and 7.2 weight per cent, with ruthenium varying from 0.5 to 10 weight per cent. These data are summarized in Table 29 and, together with supplementary results from other alloys, shown in Figure 35.

Table 29

THE CHANGE IN MOLYBDENUM Kα X-RAY INTENSITY WITH RUTHENIUM CONTENT IN TERNARY URANIUM ALLOYS

(Tungsten tube at 57 kvp, 44 ma; topaz analyzer; 800:1 collimator; Kr-filled Geiger Counter)

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Weight Per Cent (by chemical analysis)</th>
<th>Intensity (cps) at 30.35°θ (126000 counts)</th>
<th>Change in MoKα Intensity per Unit Increase in Ru Weight Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>Ru</td>
<td>MoKα + ULβ + Background</td>
</tr>
<tr>
<td>Unalloyed U</td>
<td></td>
<td></td>
<td>359</td>
</tr>
<tr>
<td>FST-1-B</td>
<td>2.42</td>
<td>0.51</td>
<td>673</td>
</tr>
<tr>
<td>FST-4-B</td>
<td>2.42</td>
<td>5.86</td>
<td>685</td>
</tr>
<tr>
<td>FST-9-B</td>
<td>2.40</td>
<td>10.06</td>
<td>689</td>
</tr>
<tr>
<td>15 EA</td>
<td>5.75</td>
<td>2.66</td>
<td>1068</td>
</tr>
<tr>
<td>FST-5-T</td>
<td>5.82</td>
<td>5.73</td>
<td>1091</td>
</tr>
<tr>
<td>FST-7-T</td>
<td>5.67</td>
<td>7.99</td>
<td>1105</td>
</tr>
<tr>
<td>FST-6-T</td>
<td>5.73</td>
<td>9.98</td>
<td>1116</td>
</tr>
<tr>
<td>FST-2-B</td>
<td>7.17</td>
<td>0.49</td>
<td>1212</td>
</tr>
<tr>
<td>1A-1</td>
<td>7.15</td>
<td>5.72</td>
<td>1274</td>
</tr>
</tbody>
</table>

These alloys may be referred to as ternaries in this connection since the matrix effect of the minor constituents in typical "fissium" alloys can be ignored.

The intensity at 30.35° minus the intensity from unalloyed uranium at this angle is taken as the MoKα intensity.
as a family of typical working curves for direct molybdenum analysis. With "fissium" alloys containing zirconium the molybdenum Kα X-ray is absorbed even less by the zirconium atoms than by ruthenium atoms; nevertheless, by means of the family of working curves based on uranium-molybdenum-ruthenium alloys it has been shown that ruthenium can serve as a rather good stand-in for zirconium when the per cent molybdenum in uranium-molybdenum-ruthenium-zirconium alloys is desired.

For the case of direct determination of ruthenium in "fissium," it would be expected that the ruthenium Kα X-ray would be absorbed less by uranium than is the molybdenum Kα X-ray so that, as uranium atoms are replaced by molybdenum atoms in the matrix, the effect on the fluorescent X-ray intensity from a given weight per cent of ruthenium would be less noticeable than the ruthenium content effect on molybdenum Kα, summarized in Table 29; correspondingly, it should be even more apparent at very low concentrations where matrix atoms are overwhelming. In Table 30 the data obtained at 0.5 weight per cent ruthenium show a discernible increase in ruthenium Kα intensity with increase in weight per cent molybdenum or, alternatively, decrease in uranium. At 6 per cent and 10 per cent ruthenium this molybdenum content effect on ruthenium Kα did not appear. When zirconium also is present and when the interaction coefficients are not determined, uranium in uranium-molybdenum-ruthenium standards would be a better stand-in for zirconium than would molybdenum, though not as good as ruthenium for zirconium in the molybdenum analysis described above. The reliability of this method for ruthenium in the composition range 0.5 to 6 weight per cent can equal that for molybdenum in the range 1.5 to 7.5 per cent when the calibrating alloys can be equivalently standardized.

Zirconium in uranium-"fissium" alloys was detected directly with high analytical sensitivity. However, the inter-element effects in this system include enhancement of the zirconium Kα X-ray intensity by the presence of ruthenium, in addition to the large decrease in absorption for zirconium Kα as uranium atoms are replaced by molybdenum and/or

![Figure 30](image)
ruthenium atoms. Accordingly, when more than a relative criterion for zirconium concentration is needed, the interaction coefficients of the system must be determined in order to attain high analytical reliability. A generalized calibration may be made for wide applicability.

Table 30

THE EFFECT OF MOLYBDENUM CONTENT ON RUTHENIUM Ka X-RAY INTENSITY FROM TERNARY URANIUM ALLOYS

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Ru (by chemical analysis)</th>
<th>Mo (by chemical analysis)</th>
<th>Intensity (cps) at 27.47° 2θ (64000 counts)</th>
<th>Change in RuKa intensity per unit increase in Mo weight per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unalloyed U</td>
<td>-</td>
<td>-</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>SNT-27</td>
<td>0.50</td>
<td>1.00</td>
<td>141.5</td>
<td>61.5, +1.8</td>
</tr>
<tr>
<td>FST-1-T</td>
<td>0.50</td>
<td>2.38</td>
<td>143</td>
<td>63, +1.8</td>
</tr>
<tr>
<td>SNT-25</td>
<td>0.49</td>
<td>4.98</td>
<td>146</td>
<td>66, +1.6</td>
</tr>
<tr>
<td>FST-3-T</td>
<td>0.49</td>
<td>9.74</td>
<td>151</td>
<td>71, (less than the counting error)</td>
</tr>
<tr>
<td>FST-4-B</td>
<td>5.85</td>
<td>2.42</td>
<td>735</td>
<td>655, (less than the counting error)</td>
</tr>
<tr>
<td>FST-5-B</td>
<td>5.87</td>
<td>5.48</td>
<td>741</td>
<td>661, (less than the counting error)</td>
</tr>
<tr>
<td>FST-8-B</td>
<td>5.88</td>
<td>13.3</td>
<td>738</td>
<td>658, (less than the counting error)</td>
</tr>
<tr>
<td>FST-9-B</td>
<td>10.00</td>
<td>2.40</td>
<td>1143</td>
<td>1063, (negligible)</td>
</tr>
<tr>
<td>FST-10-B</td>
<td>10.04</td>
<td>6.92</td>
<td>1149</td>
<td>1069, (negligible)</td>
</tr>
</tbody>
</table>

These alloys may be referred to as ternaries in this connection, since the matrix effect of the minor constituents in typical "fissium" alloys can be ignored.

The intensity at 27.47° minus the intensity from unalloyed uranium at this angle is taken as the RuKa intensity.
VII. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste Processing Operations

(J. Harast, K. Bremer, D. Turner, F. Testa, C. Ryberg)

A total of 41,500 gallons of radioactive liquid wastes was processed during this quarter as compared to 43,200 gallons in the previous quarter. Of this amount, 24,700 gallons were processed by evaporation, 1400 gallons concentrated, 4500 gallons filtered, 5000 gallons flocculated, 500 gallons absorbed into Vermiculite, 20 gallons distilled and 5400 gallons containing Na\textsuperscript{22} pumped into holding tanks to allow for decay.

B. Gamma-Irradiation Facility

(H. G. Swope, J. Harast, R. Juvinall, N. Ondracek, J. Gates, B. Kullen)

There were a total of 3042 samples, each equivalent to a No. 2 sized can, irradiated during the present quarter, an increase of 37 per cent over the previous quarter. In addition, 1183 special dosimetry samples were irradiated in the M-1 rack.