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**AEC Research and
Development Report**

Argonne National Laboratory

CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

July, August and September, 1956

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for Plutonium and Uranium
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ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, and September, 1956

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December, 1956

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

for July, August, and September, 1956

SUMMARY

I. Solvent Extraction - Study of Dispersion and Coalescence (page 13)

Additional runs have been made in the six-inch, continuous-flow mixing chamber to study the rate of mass transfer between isobutanol and water. These runs were inconclusive because the effluents were mutually saturated. A new four-inch cell has been designed and is being fabricated; this will permit a reduction in the time available for mass transfer. Consideration has been given to other liquid pairs which may transfer more slowly than isobutanol-water. The system nitrobenzene-ethylene glycol appears attractive.

II. Fluoride Volatilization Separations Process (pages 14 to 53)

Developmental work has continued on the processing of zirconium-uranium fuel alloys in fused fluoride systems. Further corrosion tests were performed on graphite, which appears to be the most suitable container material for the dissolution step.

The behavior of plutonium during the uranium volatilization step of the fused salt process was examined in the laboratory. Only negligible amounts of plutonium were removed from the melt by sparging it with bromine pentafluoride vapor at 600 C.

Studies have been continued on the development of a scheme by which uranium-plutonium alloys might be processed in fluoride systems. Further data were obtained on the rates of fluorination of plutonium tetrafluoride by fluorine. Uranium-plutonium alloys were found to react smoothly in liquid bromine trifluoride. After the volatile products of the reaction and the excess bromine trifluoride were removed by distillation, the plutonium in the residue was volatilized by fluorination.

Crude uranium tetrafluoride produced from ore concentrates by hydrogenation and hydrofluorination in fluidized bed reactors was converted to the hexafluoride in a small-scale fluidized bed.

The separation of small amounts of molybdenum hexafluoride from uranium hexafluoride by distillation was demonstrated by a tracer technique.

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This information is pertinent to fuel processing in which molybdenum appears as a fission product and to feed material operations where it is present as an impurity.

Kinetic data were obtained on the gas-phase reaction between fluorine and bromine trifluoride to produce bromine pentafluoride. Thermodynamic information was gained from measurements of chemical equilibrium on the gaseous system bromine-bromine trifluoride-bromine monofluoride. This information was used to calculate the standard enthalpy and free energy of formation for bromine trifluoride. Theoretical and experimental evidence indicated that bromine does not react appreciably with bromine pentafluoride at 75°C.

A sixth pilot plant run was completed, using 14 kg of 430 g/t Hanford-irradiated natural uranium which had been cooled 80 days. The product uranium hexafluoride contained fission product activity of the order of one to ten per cent the activity of aged unirradiated natural uranium. The indicated decontamination factors were of the order of 10^8 or greater.

Two runs were made to determine the separation of molybdenum and vanadium fluorides from uranium hexafluoride. A charge containing 460 ppm molybdenum and 31 ppm vanadium was reduced to ~ 1 ppm each. The fluorides of both molybdenum and vanadium are more volatile than uranium hexafluoride.

III. Fluidization (pages 54 to 70)

Fluidization process studies during this quarter were concentrated primarily on the development of the fluorination process for refining uranium ore concentrates. In addition to experiments with South African Rand ore concentrate, studies were carried out on the preparation of crude green salt from five different types of domestic ore concentrates. Several of these concentrates were found to consist of very fine, non-fluidizable powders. A technique for converting these powders to a fluidizable size by briquetting, crushing, and screening was developed.

Reduction and hydrofluorination experiments showed that the domestic ore concentrates were less reactive than Rand material, but the degree of conversion to crude green salt obtained is considered adequate for these intermediate process steps.

Installation of the green salt pilot plant was nearly completed, and initial testing of the "hydraulics" of the system was started using uranium trioxide as the solid phase and air as the gas phase.

Fabrication of the fluidized-bed calciner for reactor fuel processing wastes was completed and installation of this unit in a shielded cell was started.

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Work on the fundamental study of fluidization characteristics of particle mixtures was centered on eliminating the effect of static electricity, which is believed to be the cause of the non-reproducible data obtained. The use of graphite particles in place of glass beads has yielded improved data.

IV. Reactor Chemistry (pages 71 to 90)

The absolute fission yield of cesium-137 has been determined for fast neutron fission of uranium-235 and plutonium-239. The number of fissions was determined by absolute counting of the fission fragments. The cesium-137 activity was determined by absolute counting with an end-window proportional counter. The yields were found to be 6.87 per cent and 7.45 per cent for uranium-235 and plutonium-239, respectively. These values are based on a cesium-137 half-life of 32.6 years.

Samples of uranium-235, plutonium-239 and uranium-238 have been exposed in various parts of EBR-1 in order to determine the variation of alpha, the ratio of capture to fission cross sections, with reactor position. These samples were exposed during the second loading of EBR-1. The uranium-235 and the plutonium-239 samples have been analyzed radiochemically to determine the burn-up, i.e., the fraction fissioned, and mass spectrometrically to determine the fraction which has undergone the capture process. The results are presented graphically. Analyses of uranium-238 data are not yet complete.

The study of the oxidation characteristics of uranium, thorium, zirconium and plutonium has been continued. It is felt that conditions which accelerate the oxidation rates will lower the ignition temperatures and increase the possibility of spontaneous ignitions. Thus, an understanding of the kinetics of oxidation and the mechanism of the reaction should help predict when these metals will be unusually sensitive to spontaneous ignition.

V. Chemical-Metallurgical Separation Processes (pages 91 to 136)

The activation energy for the attack of liquid uranium on high purity, high density alumina is 48.2 ± 0.6 kcal/mole. The rate of attack on thoria or beryllia increases with exposure.

The extraction of plutonium from hydride-produced 1% plutonium-uranium powder by molten magnesium has been shown to proceed with good efficiency.

Data have been obtained for the partition of ruthenium between liquid magnesium and liquid uranium-iron alloy. The distribution is highly in favor of the heavy metal phase and shows significant variations with temperature and concentration.

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Testing of pilot plant equipment components was continued. Analyses of small protrusions cast on poured ingots were in agreement with analyses of the melt and indicate protrusion casting to be a feasible sampling procedure. Two-kilogram charges of sodium-coated uranium pins, which simulate discharged fuel material, were satisfactorily melted.

Work has been started on the purification of uranium from noble fission products by fractional crystallization from a solvent metal such as zinc.

Four successive magnesium extractions of plutonium from a uranium-chromium-plutonium alloy resulted in the extraction of 85 per cent of the plutonium. A five-kilogram scale batch extraction unit has been installed and preliminary testing begun.

Oxidation of sodium-coated uranium pins at 600 C in a 1000 ppm oxygen in argon atmosphere was found to be excessive. Consequently, the oxygen impurity concentration in the cell atmosphere must be maintained at a considerably lower concentration (~ 20 ppm) than 1000 ppm.

Studies of inert gas purification show that oxygen may be completely removed from argon by reaction with hydrogen previously sorbed on a 0.5 per cent palladium on alumina catalyst. Although nitrogen removal from the cell atmosphere by chemical means may not be necessary, it was shown that the use of hot calcium at 600 C or sodium-activated calcium at 440 C is effective.

VI. Analytical Research and Services (pages 137 to 146)

An X-ray spectrometric method is being developed for rapid, convenient determination of plutonium in the concentration range 3 to 9×10^{-3} M. One-half ml of solution is used for each determination, so that the total plutonium requirement is between 0.35 to 1 mg. Counting times range from two to four minutes.

Additional non-radioactive alloys representative of high burn-up reactor fuels have been obtained and examined in order to define more carefully some of the factors in the X-ray spectral method for molybdenum and ruthenium in a uranium matrix.

VII. Routine Operations (page 147)

The operation of the radioactive liquid waste facility and the gamma irradiation facility continued without incident.

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I. SOLVENT EXTRACTION - STUDY OF DISPERSION AND COALESCENCE

(W. A. Rodger, V. G. Trice, Jr., L. F. Dorsey)

Additional runs have been made in the six-inch, continuous-flow mixing chamber to study the rate of mass transfer between isobutanol and water. These runs were inconclusive because the effluents were mutually saturated. A new four-inch cell has been designed and is being fabricated; this will permit a reduction in the time available for mass transfer.

Light scattering-interfacial area correlations have been reported previously for 50 and 25 per cent dispersions. This phase of the work will be terminated with the development of correlations for 10 per cent dispersions. Several runs have been made to obtain the required data.

The results of most of the mass transfer runs have been disappointing because, within the limits of the experimental techniques, the effluent streams have been mutually saturated. This difficulty may be alleviated by reducing the surface area and/or contact time, or by substituting for isobutanol-water a system which transfers more slowly. Each of these alternatives has been or will be investigated.

The preliminary series of runs showed that the surface area produced, which averaged 150 sq cm per cu cm, was larger than expected. Furthermore, repeated reuse of the isobutanol resulted in a progressive increase in the interfacial area caused by the accumulation of surface contamination. The incorporation of a solvent clean-up distillation step did decrease the interfacial area to about 130 sq cm per cu cm, but not enough to give reproducible results. The limited capacity of the influent pumps prevented the reduction of contact time by increasing the influent flow rate. A four-inch mixing chamber was, therefore, designed to replace the six-inch unit currently in use. The new unit will afford a 70 per cent decrease in contact time.

Consideration has been given to other liquid pairs which may transfer more slowly than isobutanol-water. Some investigators have suggested that the Schmidt number (ratio of viscosity to the product of density and diffusivity) varies inversely with the mass transfer coefficient. From that point of view the system nitrobenzene-ethylene glycol, which has a Schmidt number 20 times that of isobutanol-water, appears very attractive. A limited number of runs will be made with this system.

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II. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

Development work has continued on the processing of zirconium-uranium fuel alloys in fused fluoride systems. The alloy is dissolved by hydrofluorination in molten sodium fluoride-zirconium fluoride at 600 C. The melt is then sparged with fluorine or bromine pentafluoride vapor, volatilizing the dissolved uranium as the hexafluoride. This product is purified and decontaminated by fractional distillation.

Further corrosion tests were performed on graphite, which appears to be the most suitable container material for the dissolution step. Various metals were also examined to determine their characteristics as back-up materials for a graphite dissolver.

The behavior of plutonium during the uranium volatilization step of the fused salt process was examined in the laboratory. Only negligible amounts of plutonium were removed from the melt by sparging it with bromine pentafluoride vapor at 600 C.

Studies have been continued on the development of a scheme by which uranium-plutonium alloys might be processed in fluoride systems. Further data were obtained on the rates of fluorination of plutonium tetrafluoride by fluorine. Uranium-plutonium alloys were found to dissolve smoothly in liquid bromine trifluoride. After the volatile products of the reaction and the excess bromine trifluoride were removed by distillation, the plutonium in the residue was volatilized by fluorination.

Crude uranium tetrafluoride produced from ore concentrates by hydrogenation and hydrofluorination in fluidized bed reactors was converted to the hexafluoride in a small-scale fluidized bed. Fluorine, diluted with nitrogen, was passed through beds containing mixtures of calcium fluoride and the crude uranium tetrafluoride. A semi-continuous method of operation proved feasible in the laboratory.

The separation of small amounts of molybdenum hexafluoride from uranium hexafluoride by distillation was demonstrated by a tracer technique. This information is pertinent to fuel processing in which molybdenum appears as a fission product and to feed material operations where it is present as an impurity.

Kinetic data were obtained on the gas-phase reaction between fluorine and bromine trifluoride to produce bromine pentafluoride. Thermodynamic information was gained from chemical equilibrium measurements on the gaseous system bromine-bromine trifluoride-bromine monofluoride. This information was used to calculate the standard enthalpy and free energy of formation for bromine trifluoride. Theoretical and experimental evidence indicated that bromine does not react appreciably with bromine pentafluoride at 75 C.

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A sixth pilot plant run was completed using 14 kg of 430 g/t Hanford-irradiated natural uranium which had been cooled 80 days. The product uranium hexafluoride contained fission product activity of the order of 1 to 10 per cent the activity of aged unirradiated natural uranium. The indicated decontamination factors were of the order of 10^8 or greater.

Two runs were made to determine the separation of molybdenum and vanadium fluorides from uranium hexafluoride. A charge containing 460 ppm molybdenum and 31 ppm vanadium was reduced to ~ 1 ppm each. The fluorides of both molybdenum and vanadium are more volatile than uranium hexafluoride. The vanadium result was not expected from meager literature data, and the properties of vanadium fluorides are being investigated by the laboratory group.

The fused-salt equipment was given shakedown tests in the current period.

The work of the group was discussed during this quarter with representatives of Horizons, Inc., the French Atomic Energy Group, Union Carbide and Carbon, Oak Ridge National Laboratory, Phillips Petroleum and the Allied Chemical and Dye Corporation.

A. Laboratory Investigations
(R. K. Steunenberg)

1. Fused Salt Processing of Enriched Reactor Fuels

a. Corrosion Investigations
(W. B. Seefeldt, S. Vogler, L. Hays, R. L. Breyne,
G. W. Redding)

Corrosion testing of several materials in fused fluoride melts sparged with hydrogen fluoride and bromine pentafluoride has been continued. Unless otherwise noted, all the tests were conducted at 600 C in an equimolar sodium fluoride-zirconium fluoride melt. Tests made during the quarter can be placed in the following four groups:

- (1) Corrosion tests were made on graphite in the hydrofluorinated melt to determine the performance of various graphite grades in the conventional liner-impingement plate configuration (see ANL-5602, Figure 5).
- (2) Metal life tests were made on the hydrofluorination of low-carbon nickel and Monel liners to determine their tendency toward embrittlement relative to that of "A" nickel.

- (3) Tests were conducted to determine the degree of carburization of metals in contact with graphite in the absence of the fused salt. Resistant metals could be considered for prospective use as back-up metals for graphite liners.
- (4) Two miscellaneous tests were made, in one of which several types of Kennametal were hydrofluorinated in the fused salt. In the other, miscellaneous test mild steel was subjected to a sparge of bromine pentafluoride vapor in the melt.

1. Graphite Tests

The testing of graphite in the fluorination step of the fused fluoride process was continued and standardized by using impingement plates and crucibles made from the graphite under test. Corrosion rates of the graphite were determined from the dimensional changes of the sparge plates and crucible walls. Additional types of graphite were tested. Also, the effects of uranium in the melt, longer periods of exposure, higher melt temperatures and thermal cycling of the melt were investigated.

The data are tabulated in Table 1. The following procedure was used to compute the corrosion. Six equally spaced holes had been drilled in each impingement plate prior to the test (ANL-5602, Figure 5). This plate was examined under a microscope (45X) and the hole diameter measured by a scale in the eyepiece. Each hole was measured twice, giving a total of twelve measurements. The averages of the measurements before and after exposure to the fused salt were compared to give an average corrosion rate for the experiment. One-half the difference of the diameters was taken as the corrosion rate of the graphite. Several series of measurements indicated a standard deviation of 0.8 per cent. For a seven-day corrosion test this error would amount to a total penetration of approximately ± 0.4 mil. Most of the data indicated in Table 1 are therefore close to the limit of error of measurement.

It is of interest that the two-week exposures resulted in absolute measurements about the same as for the shorter runs. Thus it is quite probable that the corrosion of graphite as indicated by enlargement of the impingement plate holes is considerably less than 0.8 mil per week on a continuing basis.

Caliper measurements were also made on the impingement plate diameters and thicknesses and on the outside diameters of the gas entry tubes. In most cases the readings were identical before and after exposure. In some cases readings of several tenths of a mil were obtained

Table 1

GRAPHITE CORROSION IN EQUIMOLAR SODIUM FLUORIDE-ZIRCONIUM FLUORIDE MELTS

New graphite crucibles were used for each run and were fabricated (1-5/16 inches OD x 7-1/2 inches) to fit inside the nickel crucible in the apparatus shown in ANL-5494, page 34. Impingement plates are shown in ANL-5602, page 18.

Run No.	Graphite Type ^d	Max Grain Size (inch)	Density (g/cc)	Temp. (C)	HF Gas Flow (g/hr)	Time (weeks)	Dimensional Change (mils) ^c		
							Impingement Plate Hole Diam.	I.D. Gas Entry Tube	Crucible Wall Thickness
68	CS	0.031	1.67	600	39.3	2	0.0	0.7	0.7
69	CS ^a	0.031	1.67	600	15.1	1	0.07	0.5	2
72	CS	0.031	1.67	800	26.9	1	0.1	0.5	2.4
71	CS	0.031	1.67	600-90	Helium 100 cc/min ^b	1	0.9	2	2
70	ATZ	0.006	1.70	600	18.9	1	2	2	0.3
74	AGR	0.016	1.57	600	31.0	1	0.2	0.7	0.8
76	AGR	0.016	1.57	600	46.9	1	0.2	0.7	0.5
79	HC	0.03	1.56	600	12.3	1	0.5	0.7	3
80	HLM	0.03	1.67	600	26.9	1	0.6	0.4	1
82	HPC	0.03	1.67	600	47.5	1	0.1	0.3	1

^aUF₄ (1 weight per cent) was added to the melt.

^bThe thermal cycling was carried out by heating for three hours and then allowing the furnace to cool for three hours. At the end of the cooling period, the temperature had reached 90 C. After one hour of heating, the furnace was at full temperature. Thus at the end of one week, 28 cycles were completed.

^cThe dimensional changes are the increases in the hole diameters of the impingement plate holes and the gas entry line and the decreases in wall thickness of the crucible. These data assume a uniform rate of attack. The precision of the measurements of the impingement holes is 0.8 mil, so that smaller values are of doubtful meaning. The corrosion penetration would then be one-half of the dimensional change. For a one week exposure, these values would show a linear corrosion of approximately 0.06 mil/day.

^dGraphite type denotes the identification given the various grades of graphite by the manufacturer. For example, CS, ATZ and AGR are products of the National Carbon Company and HC, HPC and HLM are products of Great Lakes Carbon Company.

for a one-week exposure. The corrosion of the crucible wall appeared to be somewhat greater than that of the impingement plate. In all cases, however, the corrosion rates were low, indicating that graphite should be a satisfactory material for the hydrofluorination step.

graphite tests: Additional specific observations were made during the

In Runs 68 and 69, it was noted that very little salt had penetrated the walls of the crucible and the machine markings on the graphite were still evident. Again in Runs 71 and 72 very little melt penetrated the crucible, apparently just enough to form a thin film on the outside wall. The outside of the crucible from Run 72 was somewhat roughened, possibly due to increased oxidation of the graphite at the elevated temperature.

In Run 70, the rate of attack was somewhat higher than normal. When the exposure was completed, some melt was allowed to solidify in the crucible. After standing at room temperature for two days, the crucible cracked in two places. One crack appeared at the bottom, the other where the melt interface had been. An examination of the crucible walls along the cracks showed the presence of solidified melt in the graphite voids, although very little melt had actually penetrated the crucible during the run.

In another run with ATZ graphite it was found after two days of testing that the sparge tube had slipped from the metal coupling into which it had been screwed. The coupling was covered with salt, and it was discovered that marked thinning of the graphite sparger wall had occurred. These difficulties with the ATZ graphite might suggest that fine-grained graphite is not necessarily the best type to use with the fused fluoride melt.

The results indicate that graphite is satisfactorily resistant to chemical corrosion by hydrofluorination in the fused fluorides. Certain problems may arise, however, in connection with its mechanical properties.

2. Metal Life Tests

Several life tests were conducted with low-carbon nickel and Monel. Only liners were used in the tests, and these were tested until failure.

The test data are given in Table 2. Observations during these tests are as follows:

- (1) Run 64; low-carbon nickel. A low-carbon nickel with a wall thickness of 50 mils was tested. Failure occurred after exposure for 629 hours, apparently through weakening due to loss of ductility. A photograph of the failed liner is shown in Figure 1. Metallographic examination revealed severe intergranular surface attack, but there was little penetration of this attack into the metal (a maximum of 5 mils). Further examination revealed grain size differences in the hot zone of the liner. It appeared that grain growth had progressed from the outer surface inward in a regular manner. Three-fourths of the wall at the bottom consisted of large grains, and this fraction decreased with elevation until at a height of $2\frac{1}{2}$ in. the entire section showed normal grain size. It is probable that the loss of ductility which caused the failure was a result of grain growth rather than intergranular penetration.

The maximum corrosion occurred at a height of $1\frac{1}{4}$ in. This corresponds to the height of the impingement plate, where the sparge gas is forced outward against the liner wall. The total penetration was 32 mils; assuming linear corrosion over the test period, this corresponds to a rate of 1.2 mils per day.

- (2) Run 78; low-carbon nickel. A 32-mil liner was tested to determine whether the wall thickness had a profound effect on the liner life. Failure occurred after 408 hours. A section of the liner wall showed that the failure probably resulted from a reduction in the wall thickness, since the areas adjacent to the failure measured 2 to 4 mils. As in Run 64, metallographic examination revealed severe intergranular attack, but this attack did not extend more than several mils below the surface. Grain sizes in the liner wall were uniformly small; no obvious grain growth had appeared. The maximum attack of 32 mils at the point of failure corresponds to a linear corrosion rate of 1.9 mils per day.

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Table 2

RUN CONDITIONS FOR METAL-LIFE CORROSION TESTS

Melt: Equimolar sodium fluoride-zirconium fluoride
 Temperature: 600 C
 Melt Weights: 300 - 350 grams
 Cross-sectional Area of Liner: 1.62 in.²
 Sparge Gas: HF

Run No.	64	78	73
Material	low-carbon nickel	low-carbon nickel	Monel
Wall Thickness (inch)	0.050	0.032	0.032
Average Sparge Rate, gms/hr	32	52	57
Test Time, hours	629	408	780 ^a

^aTest is still running.

FIGURE 1.

FAILURE OF LOW CARBON NICKEL DUE TO INTERGRANULAR ATTACK.

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These two tests with low-carbon nickel indicate that it is superior to "A" nickel in resisting intergranular weakening; like "A" nickel, however, it is susceptible to weakening by loss of ductility resulting from grain growth.

- (3) Run 73; Monel. At the conclusion of the report period a 32-mil Monel liner had been under test for 780 hours without failure. Since the original Monel sparger and impingement plate had plugged after 300 hours, they were replaced. The second one is still operating.

Observations were made on the original Monel sparger which had plugged. The tip of the gas outlet tube was still nearly square. A cross section of the tip showed voids on the inner surface to a depth of 4 mils, and on the outer surface to a depth of 1 mil. These voids were presumed to be areas from which copper had been removed selectively. Higher up on the sparge tube, the depletion layer on the inside decreased to zero, while that on the outside increased to about 3 mils. No obvious intergranular attack was revealed by metallographic examination, nor was there any evidence of grain growth.

Dimensional change data for this Monel sparge tube and impingement plate assembly are summarized in Table 3.

3. Carburization Tests

In order to determine what materials might be used to back up graphite, a carburization test was started. Seven metals were packed in powdered graphite and heated to 600 C under a helium atmosphere. After three weeks, slices were cut from the coupons and evaluated for depth of carburization. The remaining portions of the coupons along with new coupons of Types 309 and 310 stainless steel were returned to the test. The three-week evaluations are as follows:

- (1) Type 347 Stainless Steel: very small particles of graphite noted along both edges to a depth of 0.12 to 0.15 mil. Local attack to 0.38 mil.
- (2) Monel: very thin lines of penetration visible, probably along grain boundaries. Maximum depth observed: 1.1 mils.

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Table 3

RATES OF PENETRATION OF MONEL IN HYDROFLUORINATED FUSED FLUORIDE MELTS

Temperature: 600 C
Test Component: Sparge tube and impingement plate
Run: 73
Exposure Time: 300 hours

<u>Description</u>	<u>Dimensional Change, mils</u>	<u>Rate of Penetration, mils/day</u>
Maximum sparge tube attack below impingement plate.	14	1.1
Maximum sparge tube attack above impingement plate.	18	1.4
Interface attack	8	0.6
OD of impingement plate	4	0.3
Thickness of plate	5	0.4
Plate holes OD, maximum	4.4	0.35
minimum	2.5	0.2

- (3) Inconel: carburized layer on one surface about 0.15 mil uniformly along the surface. Local attack up to 1 mil. Local attack more frequent but not as deep on the opposite surface.
- (4) Type 330 Stainless Steel: thin layer 0.12 mil deep on all exposed surfaces. Heavy intergranular carburization evident on both edges. Maximum depth: 1.5 mils.
- (5) Nickel: heavy lines of attack at isolated locations. Depth: 0.67 mil.
- (6) Type 304 Stainless Steel: uniform carburized layer of 0.12 mil. Local penetration to 0.5 mil.
- (7) Hastelloy B: no visible attack.

4. Miscellaneous Tests

- (1) Run 77; Kennametal. Two sample pieces of Kennametal, Types K-138A and K-151A, were subjected to hydrogen fluoride sparging in the fused fluoride

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melt. These materials consist of 10 per cent solid solution carbide (niobium, tantalum and titanium carbides), and 70 per cent titanium carbide, bonded with 20 per cent nickel or cobalt. The test period was 41 hours with an average hydrogen fluoride sparge rate of 27 g per hour. At the end of the period insufficient test material remained for evaluation.

- (2) Run 84; mild steel. In another test mild steel was exposed to a sparge of bromine pentafluoride vapor in the fused fluoride. This was the first effort to determine whether mild steel might be usable as a material of construction for a throw-away fluorination vessel. The test was started with a mild steel liner and sparger, but the latter was plugged within 5 minutes by a soft material presumed to consist of corrosion products. The mild steel sparger was replaced with nickel, and the liner was replaced by a 32-mil mild steel sheet rolled inside the nickel liner, thus eliminating the problem of exterior oxidation. The results of sparging for 6-1/2 hours with bromine pentafluoride at an average rate of 61 g per hour are shown below.

Maximum attack (at interface):	9 mils
Attack in liquid phase:	4-5 mils
Attack in vapor phase:	2-5 mils

The melt used in the test became very discolored.

5. Mechanism

It had been reported previously (ANL-5602, page 30) that "A" nickel samples from three tests in molten sodium fluoride-zirconium fluoride had been submitted to the International Nickel Company for evaluation in their laboratories. The sparge gases used in these runs were helium, hydrogen and hydrogen fluoride, respectively. The first two samples showed no metal weakening, while severe intergranular attack was found in the third. The laboratory evaluations indicated no adverse structural effects in the first two samples. The conclusion regarding the third sample was as follows: "There seems to be no question that the embrittlement is due to sulfur and that the source of this impurity is the hydrogen fluoride sparge gas." This conclusion was based on metallographic evidence.

At the suggestion of J. Draley of the Metallurgy Division Corrosion Group, an embrittled and an unexposed piece of nickel were analyzed for hydrogen in the hope that if a hydrogen mechanism were responsible for the embrittlement, it might be shown by a chemical analysis. The analyses, performed by W. Ruther of the Corrosion Group, gave the following results:

Unexposed nickel: 0.5 ppm hydrogen
Embrittled nickel: 0.4 ppm hydrogen.

No additional data relative to mechanism studies were obtained during the period.

b. Behavior of Plutonium During the Volatilization of Uranium Hexafluoride
(S. Vogler)

Only small amounts of plutonium are produced by highly enriched reactor fuels. While its recovery is not required, it must be separated from the uranium. Since plutonium is known to form a volatile hexafluoride analogous to the uranium compound, it was of interest to determine whether it would be volatilized during the bromine pentafluoride sparging operation.

The equipment used in the experiments was similar to that used to demonstrate uranium recovery, except that it was smaller. The dissolver vessel was a 3/4-inch nickel tube attached to the line by a flare fitting. The equipment is shown schematically in Figure 2. In order to simplify the operation, uranium-plutonium alloy was dissolved in equimolar sodium fluoride-zirconium fluoride by a bromine pentafluoride sparge. Previous experiments (ANL-5422, page 29) had indicated that uranium dissolves readily under these conditions and that quantitative uranium recovery is achieved within one hour.

The procedure was as follows. Forty grams of equimolar sodium fluoride-zirconium fluoride were placed in the 3/4-inch nickel dissolver. When the salt was molten, the tube was fastened to the line and bromine pentafluoride vapor was passed through the melt for one hour at 600 C to fluorinate the melt and equipment. After the prefluorination the furnace tube was lowered to permit the addition of the uranium-plutonium alloy. The tube was attached to the line again, and bromine pentafluoride vapor was passed through the melt at 600 C for two hours at a rate of approximately 18 g/hr. The bromine pentafluoride and uranium hexafluoride were collected in cold traps at -30 C. At the completion of the run, the melt and the contents of the first trap were sampled and assayed for uranium and plutonium. The results of two experiments of this type are given in Table 4. It is believed that the plutonium material balance was high due to

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FIGURE 2.

APPARATUS FOR PLUTONIUM VOLATILITY EXPERIMENT.

Table 4

VOLATILITY OF PLUTONIUM FROM EQUIMOLAR ZIRCONIUM FLUORIDE-
SODIUM FLUORIDE MELTS WITH BROMINE PENTAFLUORIDE

Source of Plutonium: Plutonium-Uranium Alloy (0.92% Plutonium)
 Temperature: 600 C
 Time: 2 hours
 Melt: 40 g Equimolar NaF-ZrF₄

Exp. No.	Wt. Sample (g)	BrF ₅ Rate (g/hr)	Per Cent Found				Per Cent Remaining in Melt	
			First Trap		Second Trap			
			U	Pu	U	Pu	U	Pu
1	0.548 ^a	24.5	83.1	-	6.3	-	0.05	-
2	0.43	17.5	85.9	0.02	4.7	0.004	0.7	167 ^b
3	0.45	18.5	105.	0.03	6.8	0.002	0.3	168 ^b

^a Uranium tetrafluoride was the source of uranium in this first test run.

^b The high percentage for plutonium may be due to a poor melt sample, because of melt splashing up the side of the furnace tube.

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removal of melt from the bottom of the vessel during dissolution. This arose due to solidification of melt on the upper walls of the vessel. The uranium material balance was low because the apparatus construction did not permit the lines to be washed out.

The data indicated that approximately 0.03 per cent of the plutonium was found in the cold traps. This was in agreement with the 0.01 per cent figure obtained by other workers,¹ who used fluorine instead of bromine pentafluoride.

2. Processing of Uranium-Plutonium Fuels

The scope of fluoride volatilization methods of fuel processing would be enlarged greatly if practical methods of handling uranium-plutonium alloys were developed. Such a scheme might consist of dissolution of the alloy in bromine trifluoride, the uranium hexafluoride being recovered and decontaminated by distillation. The plutonium fluorides in the residue would then be treated with fluorine, producing plutonium hexafluoride, which would also be recovered and decontaminated by appropriate volatilization techniques. Laboratory studies have been continued on the dissolution of uranium-plutonium alloy in bromine trifluoride, fluorination of the residue and handling of the plutonium hexafluoride product, with particular emphasis on its thermal stability.

a. The Thermal Stability of Plutonium Hexafluoride (M. D. Adams, D. V. Steidl)

A summary of information has been presented previously (ANL-5602, page 32) covering a series of experiments on the thermal stability of plutonium hexafluoride. These studies employed a flow system in which the plutonium hexafluoride was passed through a heated zone packed with nickel wool. In these studies the conditions of prefluorination and the decomposition temperatures were varied, and the composition was carried out in both fluorine and helium atmospheres.

These experiments involve the removal of plutonium hexafluoride from the fluorine stream by a cold trap at liquid nitrogen temperature. When the fluorine was replaced by helium and the trap was warmed, most of the plutonium hexafluoride was vaporized into the decomposition

¹ Cathers, G. I. and Bennett, M. R., "A Fused Salt-Fluoride Volatility Process for Recovery and Decontamination of Uranium," ORNL-1885 (October 10, 1955).

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zone. In the more recent experiments, however, as much as 95 per cent of the material has remained in the cold trap under these conditions. The reasons for this behavior are being investigated in an attempt to rectify the cause of this problem.

b. Rate Studies on the Fluorination of Plutonium Tetrafluoride
(M. J. Steindler, F. R. Linzer)

As indicated previously (ANL-5602, page 37), a study of the rate of fluorination of the lower plutonium fluorides has been initiated. The experimental techniques and equipment were also described, along with data on the rate of fluorination of plutonium tetrafluoride obtained from Los Alamos and Rocky Flats.

Additional data of this type have been determined, including fluorination rate studies of the residues produced by the dissolution of uranium-plutonium alloys in bromine trifluoride. The latter samples were prepared by dissolving small amounts (~ 1 g) of the alloy in approximately 9 ml of bromine trifluoride at room temperature. The volatile products were then removed by vacuum distillation.

The plutonium fluorides resulting from the alloy dissolutions were very finely divided, and X-ray examination indicated that the major product was a plutonium (IV) fluoride, probably hydrated by 0.5 to 2.0 molecules of water per molecule of plutonium fluoride. The existence of such hydrates has been indicated by other workers.² The formation of such hydrates, however, is in contradiction to statements found in the literature³ claiming that plutonium tetrafluoride does not react with atmospheric moisture under these conditions. Hydration of the tetrafluoride during its formation in a reagent such as bromine trifluoride seems highly unlikely. The very fine state of subdivision of the plutonium fluorides may have permitted the rapid uptake of atmospheric moisture at room temperature in the course of transferring the dissolution residue from the dissolving vessel to the reaction boat and the X-ray capillaries.

Recent data on the rates of fluorination of plutonium fluorides are presented in Tables 5 and 6. The data from Table 6 are plotted as a function of temperature in Figure 3 to facilitate comparison. At temperatures as low as 200 C the fluorination rates for plutonium fluorides produced by the alloy dissolutions were considerably higher than those obtained from the fluorides prepared by the usual dry process (see Figure 3). These increased rates were also evident at higher temperatures.

²Dawson, J. K., et. al., J. Chem. Soc., Part IV 3922 (1954)

³Dawson, J. K., et. al., J. Chem. Soc., Part I 558 (1954)

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Table 5

RATE OF FLUORINATION OF PLUTONIUM FLUORIDES USING GASEOUS FLUORINE

Apparatus: Nickel, Monel
Pressure: 1 atmosphere
Exposed Surface Area:^a ~2 cm²

Exp. No.	Temp (C)	Time (min)	Av Fluorine Flow Rate (cc/min)	Sample		Rate of Weight Loss (mg/hr)	Remarks
				Weight (mg)	Type		
31	200	60	95	54.1	Rocky Flats PuF ₄	3.6	
22	250	45	105	54.1	Rocky Flats PuF ₄	4.1	
33	250	45	94	49.1	Rocky Flats PuF ₄	6.4	
17	600	1.5	105	47.7	Rocky Flats PuF ₄	752	
30	200	30	112	38.5	Dissolution Residue, 5% Alloy	46.6	
18	250	20	95	41.2	Dissolution Residue, 5% Alloy	74.4	
32	300	6	220	48.2	Dissolution Residue, 5% Alloy	277	
36	300	6	246	49.5	Dissolution Residue, 5% Alloy	226	
15	375	6	175	53.1	Dissolution Residue, 5% Alloy	364	Sample partially converted to PuO ₂
23	375	5	100	42.0	Dissolution Residue, 5% Alloy	265	
26	375	6	122	45.7	Dissolution Residue, 5% Alloy	268	
29	375	6	140	87.3	Dissolution Residue, 5% Alloy	396	Large sample
20	500	1	105	39.0	Dissolution Residue, 5% Alloy	882	
19	375	15	140	54.9	PuO ₂ , formed from PuF ₄	126	
27	375	9	205	70.0	PuF ₃	117	

^aArea of the top surface of the sample, defined as the area of the opening in the top of the reaction boat.

Table 6

FLUORINATION OF PLUTONIUM TETRAFLUORIDE
IN SPECIAL CONSTANT AREA BOATS

Source of PuF_4 : Rocky Flats Exposed Area of Sample^a: 2.12 cm^2

Exp. No.	Temp. (C)	Time (min)	Av. Fluorine Flow Rate (cc/min)	Sample Weight (mg)	Rate of Weight Loss (mg/hr)
37	300	20	136	321.5	57.3
38	300	20	171	632.4	58.5
24	375	20	140	318.1	206 ^b
25	375	20	84	629.7	169 ^b

^aArea of the top surface of the sample, defined as the area of the opening in the top of the reaction boat.

^bSmall loss in handling sample probable.

FIGURE 3.
RATE OF FLUORINATION OF PLUTONIUM FLUORIDES
BY ELEMENTAL FLUORINE.

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The data in Table 6 indicate the effect of exposed sample area on the rate of fluorination. A set of special reaction boats was made in which the depth was varied, but the length and width were constant. In this way it was possible to measure the fluorination rates of samples of differing weights, but with the same exposed surface area at the top. It was found that this area was the predominant factor affecting the rate, while the sample weight had little effect. Rocky Flats plutonium tetrafluoride was used in these experiments. Some average "specific rates" observed with this material (Table 6) were 27 mg/(hr)(cm²) at 300 C and 88 mg/(hr)(cm²) at 375 C. The areas indicated are the top surface areas. These values are not regarded as final, but they may serve as a practical guide for more extensive and larger-scale studies.

3. Processing of EBR-I Core (R. K. Steunenberg, H. D. Tyler)

As a result of a power excursion in EBR-I, a portion of the core was melted, fusing the fuel elements into a mass. A few scouting experiments were conducted in an attempt to find a suitable head-end step for recovering the fissionable fuel from this material.

In order to simulate this fused material, alloys of uranium, stainless steel and zirconium were prepared by the semi-works pyrometallurgical group. Dissolution tests on this material in various aqueous solutions are indicated in Table 7. Of those solutions tested, hydrochloric acid with an oxidizing agent appears to offer the most promise.

Table 7

DISSOLUTION TESTS ON SIMULATED EBR-I FUEL IN AQUEOUS SOLUTIONS

Alloy: Uranium: 88.0 weight percent Sample Size: 3 to 6 grams
Zirconium: 2.0 weight percent Solution Volume: 100 ml
347 Stainless Steel: 10.0 weight percent

Solution	Time (hr)	Temp. (C)	Result
15 <u>M</u> HNO ₃	2	90	Little or no attack.
15 <u>M</u> HNO ₃ , 0.1 <u>M</u> HF	2	90	Little attack; green surface film.
4 <u>M</u> H ₂ SO ₄ , then H ₂ O ₂	2	100	Slow attack; H ₂ O ₂ had no effect.
4 <u>M</u> H ₂ SO ₄	4	105	Weight loss 3.4%; green residue.
6 <u>M</u> HNO ₃ , 6 <u>M</u> H ₂ SO ₄	4	50	Slow attack, residue and fragments of sample remaining.
4 <u>M</u> HNO ₃ , 4 <u>M</u> H ₂ SO ₄ , 1 <u>M</u> HF	1	100	Dissolved; much yellowish green sludge.
6 <u>M</u> HCl	0.2	25	Dissolved; greenish black residue.
6 <u>M</u> HCl, then H ₂ O ₂	0.5	25	Dissolved; trace of black residue.
5 <u>M</u> HNO ₃ , 2 <u>M</u> HCl, 0.1 <u>M</u> HF	16	25	Dissolved; trace of black residue.

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A few dissolution tests were also made with bromine trifluoride. As shown in Table 8, none of the alloys dissolved completely, and in all cases appreciable amounts of uranium remained in the residues. It was possible, however, to dissolve the residues from the bromine trifluoride treatment in 6 M nitric acid at its boiling point.

Table 8

DISSOLUTION TESTS ON SIMULATED EBR-I FUEL IN BROMINE TRIFLUORIDE

Apparatus: Fluorothene, nickel

Alloy (weight per cent)			Sample Wt. (g)	BrF ₃ (g)	Time (hr)	Av. Temp. (C)	Undissolved Alloy (g)	Uranium in Residue (per cent)
Uranium	Zirconium	347 Stainless Steel						
82.0	1.5	16.5	2.066	55	18	102	0.743	12.1
82.0	1.5	16.5	4.624	56	32	117	2.602	16.4
86.0	2.0	12.0	1.994	56	18	112	0.760	6.1
88.0	2.0	10.0	3.817	56	18	112	0.695	0.5
93.5	2.0	4.5	7.351	56	18	112	2.995	(a)

^aAnalytical result not yet available.

Neither of these studies has shown a straightforward method of processing this material in existing facilities, but the results may prove useful as a starting point in working out a suitable method.

4. Feed Materials Processing - The Conversion of Uranium Tetrafluoride to the Hexafluoride
(O. Sandus, E. J. Petkus, W. A. Shinn)

Studies have been continued on the fluidized bed conversion of uranium tetrafluoride to the hexafluoride. The uranium tetrafluoride used in the experiments had been prepared from South African Rand ore concentrate by hydrogenation and hydrofluorination in a fluidized bed reactor (ANL-5602, page 56).

Nine shakedown runs were performed in order to gain experience in operating the equipment. The reactor was made from one-inch Monel tubing with a sintered Monel filter at the top and a gas distribution plate at the bottom (see Figure 16, page 42, ANL-5602). The equipment pictured in ANL-5602 has been slightly modified by the insertion of a sodium hydroxide scrubber instead of a sodium chloride trap and the use of Drierite in the nitrogen inlet. Calcium fluoride added to the bed was found to improve the fluidization characteristics of the uranium tetrafluoride. It

also permitted the retention of a substantial portion of the bed as the uranium was removed, thereby simplifying the operation. The laboratory studies employed beds consisting of 25 weight per cent crude uranium tetrafluoride and 75 weight per cent calcium fluoride. Before fluorine was added to the system they were thoroughly mixed by fluidizing the bed with a nitrogen stream.

The experimental results are listed in Table 9.

In Run 10, about 94 per cent of the uranium was collected as the hexafluoride, with a uranium material balance of about 100 per cent. Two stoichiometric equivalents of fluorine were added separately, the collection traps being replaced between the additions. During the first addition the fluorine efficiency was about 50 per cent.

Run 11 demonstrated that practically all the uranium was removed from the bed by the addition of excess fluorine. The stoichiometric equivalent of fluorine added initially showed an efficiency of 62 per cent. Additional fluorine, corresponding to the uranium tetrafluoride remaining in the bed, again gave a 62 per cent efficiency. Excess fluorine was then passed through the bed to remove as much of the uranium as possible. About 95 per cent of the uranium was recovered as the hexafluoride as a result of the three fluorine additions. The overall uranium material balance was 100 per cent.

In Run 12, the sintered Monel filter at the top of the reactor was heated to 450 C, instead of the usual 100 C, in an effort to reduce slight caking of the material on and near the filter. When half the stoichiometric equivalent of fluorine had been added, the filter became plugged, apparently by corrosion products. Since its operation at lower temperatures had been reasonably satisfactory, the filter was used at 100 C as before in the remaining experiments.

Run 13 showed that the fluorination reaction in the fluidized bed could be operated on a semi-continuous basis to produce about 100 g of uranium hexafluoride. Nine cycles were carried out, each cycle representing the addition of a stoichiometric equivalent of fluorine, and the addition of uranium tetrafluoride to return the bed to its original composition. In the first five cycles an average fluorine efficiency of about 67 per cent was realized, the highest

Table 9

THE FLUORINATION OF CRUDE URANIUM TETRAFLUORIDE IN A FLUIDIZED BED REACTOR

Fluidized Bed Reactor: 1-inch Monel pipe
 Gas Stream: 0.073 g/min F_2 diluted with N_2 to give a
 gas flow of 1500 cc/min in the reactor
 Bed Contents: 25 wt % crude UF_4^a ; 75 wt % CaF_2 (+100 mesh)

Run No.	Initial Bed Composition		Bed Temp (C)	Fluorine Addition Data			UF_6 Produced (g)	Remarks
	CaF_2 (g)	Crude UF_4^a (g)		Stoichiometric Equivalents of Fluorine Added ^b	Time (min)	Fluorine Efficiency ^c (per cent)		
10 A	56.2	18.8	450	1	30	50	10.0	
B			450	1	30	44	8.8	
11 A	56.2	18.8	450	1	27	62	12.5	
B			450	1 ^d	29	62	-	
C			450	Excess	-	-	-	95% of UF_6 collected
12	56.2	18.8	450	$\sim 1/2$	20	-	-	Filter plugged when operated at 450 C
13 A	56.2	18.8	450	1	30	67.5	13.6	
B		e	450	1	30	68.8	13.8	
C		e	450	1	30	67.5	13.6	
D		e	450	1	30	67.5	13.6	
E		e	450	1	30	65.5	13.2	
F-I		e	450	1	30	-	-	Plug in gas distribution plate
14 A	56.2	18.8	400	1	30	52.3	10.5	
B		e	300	1	30	45.6	9.2	
C		e	200	1	30	21.5	4.3	
D		e	150	1	30	10.3	2.1	
E		e	100	1	30	0.5	0.1	

^aPurity 95.4 per cent.

^bOne stoichiometric equivalent of fluorine is that required for the reaction $UF_4 + F_2 = UF_6$.

^cFluorine efficiency is defined as $\frac{\text{moles of } UF_6 \text{ collected}}{\text{moles of } UF_6 \text{ initially present}}$ for one stoichiometric quantity of fluorine.

^dBased on the unreacted UF_4 remaining in the bed.

^e UF_4 added to restore the bed to its original composition.

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obtained in any of the runs. At the end of the fifth cycle, some plugging occurred in the gas distribution plate at the bottom of the bed. The minor difficulties encountered were believed to result from the design of the small laboratory-scale equipment.

Run 14 was performed in such a way as to indicate roughly the temperature dependence of the reaction. Operationally, the procedure was identical to that of Run 13, except that the temperature of the bed was varied. A strong temperature effect was shown by the fluorine efficiency, which dropped to 0.5 per cent at 100 C. It should be pointed out that the fluorine efficiency values cannot be interpreted as rate constants without additional data. They are intended to serve only as a general indication of the temperature effect.

X-ray analyses of the bed contents from several of the experiments indicated only minor amounts of uranyl fluoride and possibly a small quantity of U_4F_{17} . It has been stated⁴ that uranium pentafluoride and other intermediates are not formed by the fluorination of the tetrafluoride if the uranium hexafluoride is removed from the system quickly. On this basis the absence of intermediates in the fluidized bed appears reasonable.

The fluorination of crude uranium tetrafluoride in a fluidized bed appears to be practical in the laboratory. More fundamental information is needed, however, before the chemical kinetics can be understood satisfactorily.

5. The Separation of Molybdenum Hexafluoride from Uranium Hexafluoride

(L. E. Trevorrow, G. W. Redding)

The removal of small amounts of molybdenum hexafluoride from uranium hexafluoride is of importance to two different areas in which fluoride volatilization schemes might be applicable. Molybdenum appears as a contaminant of uranium ores in feed material processes and as a fission product in spent reactor fuels. The vapor pressures of the pure hexafluorides indicate that the molybdenum compound (boil pt - 35 C) is more volatile than that of uranium (subl pt - 54.6 C at 1 atm). Experiments were performed in which mixtures containing small amounts of molybdenum hexafluoride in uranium hexafluoride were partially distilled. The purpose of the study was to gain information on the basic separability of the mixture by distillation methods rather than to obtain precise measurements of the vapor-liquid equilibria.

⁴Labaton, V. Y., "A Kinetic Study of the Fluorination of Uranium Tetrafluoride by Fluorine," RDB (CAP)/R-8120 (Great Britain) (January 1955).

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The nickel vacuum apparatus used in these experiments is shown schematically in Figure 4. The technique employed was essentially a flash distillation. An appreciable fraction of the mixture was vaporized and maintained in contact with the liquid phase for some time. The vapor and liquid phases were then isolated and sampled for analysis. The system was heated to a temperature somewhat higher than that of the still pot to prevent vapor condensation and refluxing, in order to preserve the simple nature of the distillation.

FIGURE 4.

NICKEL VACUUM APPARATUS.

The molybdenum hexafluoride was prepared by direct combination of the elements. The metal was placed in the 3/4-inch nickel reaction tube and exposed to fluorine at 300 C. The molybdenum hexafluoride product was collected in tube A, which was cooled by a dry ice-trichloroethylene slush. This condensed the product, but no unreacted fluorine. The melting point of the product was 17 C (Literature values:^{5,6} 17.5 C and 17 C).

⁵ Bernhardt, H. A., Bishop, H. W. and Brusie, J. P., MDDC-1528.

⁶ Simons, J. H., "Fluorine Chemistry," Vol. I, page 112, Academic Press, New York (1950).

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The uranium hexafluoride-molybdenum hexafluoride mixture was made up in tube B, which then served as a still pot. A needle type Inconel-Constantan needle thermocouple extended to the bottom of tube B in order to record the temperature of the liquid mixture during distillation. To prepare a mixture, molybdenum hexafluoride was transferred as needed into tube B from A. Uranium hexafluoride was distilled into B on top of the molybdenum hexafluoride. Valve 3 was closed to isolate the mixture, and the system was evacuated to remove any hexafluorides remaining in the gas phase. Tube B was warmed to the equilibrium temperature and agitated occasionally to mix the components. Valves 2 and 4 were then closed and 3 was opened. The liquid temperature was maintained for periods from several minutes to over an hour. Valve 3 was closed. The material in B was frozen for a still pot sample, and the vapor in cylinder D was condensed into C for a distillate sample.

The amount of molybdenum in the two fractions of uranium hexafluoride was determined by a counting technique. Molybdenum tracer was prepared by neutron irradiation of the metal. The activity of the metal was followed for several days to verify its identity. Over a period of 476 hours, the half-life of 68 hours compared well with the literature values⁷ of 67, 64, 68.3 and 63.5 hours for molybdenum-99.

Samples from the distillation were prepared for analysis by hydrolysis in 0.5 M potassium carbonate solution. Two-milliliter aliquots of the hydrolysis solution were delivered into glass tubes and counted in a well-type scintillation counter. The well contained a lead absorber, so the beta and weak gamma activities were largely removed. By counting only the harder gamma activities of molybdenum-99, errors due to differing concentrations in the hydrolysis solutions were avoided, and the weak gamma activity of the decay product technetium-99m was absorbed. A total of at least 10^4 counts was taken on each sample. In order to correct for the normal uranium activity, pure uranium hexafluoride was distilled in the same way the mixtures had been. The still pot and distillate samples were counted, giving correction factors which were small in all the experiments, and negligible in most cases.

A uranium hexafluoride sample of 10 to 20 g was used in each experiment. The cylinder D of about 125 ml volume was included in the system to provide a vapor sample of adequate size. Since the concentration of molybdenum hexafluoride in the mixtures was only about 1000 ppm, the uranium hexafluoride in the still pot and vapor fractions could be determined by direct weighing of the samples.

⁷Hollander, J. M., Perlman, I. and Seaborg, G. T., Rev. Mod. Phys., 25, 469-651 (1953).

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The results of six experiments are given in Table 10. The net molybdenum-99 counting rates per gram of uranium hexafluoride are shown for corresponding still pot and distillate samples for a given time after separation. The separation factor is defined as the ratio of the molybdenum-99 activity per gram of uranium hexafluoride in the distillate to that in the still pot fraction.

Table 10

SEPARATION OF MOLYBDENUM HEXAFLUORIDE AND
URANIUM HEXAFLUORIDE BY DISTILLATION

Experi- ment No.	Liquid- Vapor Contact Time (min)	Still Pot Temper- ature (C)	Mo ⁹⁹ Activity		Sepa- ration Factor ^a
			Distillate (cpm/g UF ₆)	Still Pot (cpm/g UF ₆)	
1	75	88	2.80×10^5	0.343×10^5	8.15
2	160	88	3.95×10^5	1.51×10^5	2.62
3	26	88	1.64×10^5	0.643×10^5	2.55
4	70	88	1.96×10^5	0.534×10^5	3.68
5	42	110	5.2×10^5	1.41×10^5	3.7

$$^a \text{Separation Factor} = \frac{\text{cpm Mo}^{99}/\text{g UF}_6 \text{ in distillate}}{\text{cpm Mo}^{99}/\text{g UF}_6 \text{ in still pot fraction}}$$

The separation factors were all higher than the value of 1.54 at 88 C calculated from Raoult's Law. There appeared to be no explanation for the high ratio obtained in the first experiment. The other four determinations were reasonably consistent. All the data were in agreement that molybdenum hexafluoride should be removed from uranium hexafluoride effectively by fractional distillation.

6. Kinetics of the Reaction of Fluorine and Bromine
Trifluoride to Form Bromine Pentafluoride
(J. Fischer, R. K. Steunenberg, W. Lechnick)

The rate at which bromine trifluoride reacts with fluorine to produce the pentafluoride is of importance to any fluoride volatilization scheme involving bromine trifluoride. In the fused salt process for

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zirconium-uranium alloys the bromine pentafluoride used as the fluorinating agent must be regenerated from the trifluoride. For schemes in which uranium is dissolved in bromine trifluoride, this represents an unwanted side-reaction during the regeneration of the bromine trifluoride with fluorine.

The preparations of bromine pentafluoride from fluorine and bromine trifluoride and by the direct combination of the elements at 200 C were described by Ruff and Menzel.⁸ In previous work it had been observed that bromine and fluorine undergo a vigorous, complete, exothermic reaction at 25 C to form bromine trifluoride. No information has been reported, however, on the extent or kinetics of the reaction between bromine trifluoride and fluorine. The following study was made on the reaction rates of gas-phase mixtures of bromine trifluoride and fluorine.

Reagent grade bromine trifluoride was purified by redistillation in a nickel column and freed of non-condensable gases by alternate freezing and thawing under vacuum. Commercial high-purity fluorine used in the experiments was shown by analyses to have a purity greater than 99.5 per cent.

The apparatus was constructed from nickel and Monel components welded together. A 587-ml reaction vessel and a 573-ml storage and metering vessel were attached to a manifold which was provided with sources of the fluorine, bromine trifluoride, vacuum and helium. The apparatus was enclosed in a thermostatted air bath.

Pressures in the system were measured with mercury manometers used in conjunction with Booth-Cromer pressure transmitters⁹ and self-balancing relays which isolated the halogen-containing system from the manometers. Pressures in the very low ranges were measured with a thermocouple vacuum gauge. Copper-Constantan thermocouples calibrated to 0.01 degree were used to measure the temperatures.

The procedure consisted of following the reaction rate by the rate of change of total pressure when the reactants were mixed in a known volume. One of the reactant gases was added to the reaction vessel and its pressure was determined. The other gas was then added from the metering vessel, its partial pressure in the reaction vessel being calculated from the pressure decrease in the metering vessel. The usual procedure was to add the fluorine to the bromine trifluoride vapor.

⁸Ruff, O. and Menzel, W., *Z. Anorg. allgem. Chem.*, **202**, 49 (1931).

⁹Cromer, S., "The Electronic Pressure Transmitter and Self-Balancing Relay," *MDDC-803* (1947).

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The reaction was found to proceed to completion with a stoichiometric consumption of fluorine from 76 C to 105 C, as indicated in Table 11.

Table 11

STOICHIOMETRIC BEHAVIOR OF THE REACTION BETWEEN
FLUORINE AND BROMINE TRIFLUORIDE

Nickel and Monel Apparatus-Vapor Phase

Experiment	Temperature (C)	Initial Pressure		Final Total Pressure (mm)	Elapsed Time (min)
		Fluorine (mm)	BrF ₃ (mm)		
6-19	76.0	592.6	50.0	591.6	1357
6-20	76.1	591.1	49.9	591.4	320
6-21	76.0	562.2	100.1	563.6	290
6-27a	85.1	583.5	100.4	583.0	245
7-6	105.5	296.3	99.9	295.2	135

Since one mole of fluorine reacts with one mole of bromine trifluoride to produce one mole of bromine pentafluoride, the concentrations of the reactants could be calculated from the difference between the initial total pressure and the total pressure at any time. Vapor density measurements of the three compounds indicated that deviations from ideal gas behavior were within the experimental accuracy.

The reaction under consideration may be expressed as follows:

If a homogeneous, bimolecular interaction were involved, the rate of the reaction would be second-order with respect to the partial pressures of the reactants, and it could be expressed as:

$$-\frac{d[\text{F}_2]}{dt} = k[\text{BrF}_3][\text{F}_2] \quad (2)$$

An equivalent expression is

$$-\frac{dx}{dt} = k(a-x)(b-x) \quad (3)$$

where a and b are initial reactant concentrations in millimeters.

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x = decrease in reactant concentrations at a time, t .

k = second-order rate constant.

The integrated form is

$$t = \frac{2.303(a-b)}{k} \log \frac{b}{a} + \frac{2.303(a-b)}{k} \log \frac{a-x}{b-x} \quad (4)$$

Thus, a plot of t against $\log \frac{a-x}{b-x}$ should be linear.

For the case in which $a = b$, the integrated expression becomes

$$t = \frac{1}{k(a-x)} - \frac{1}{ka} \quad (5)$$

and a plot of t against $\frac{1}{a-x}$ is linear. For the case in which a and b are only approximately equal, and d is the mean initial concentration of the reactants, $\frac{a+b}{2}$, then

$$\frac{1}{d-x} - \frac{1}{d} = kt \quad (6)$$

A plot of $\frac{1}{d-x}$ against t would be linear.

In these experiments, graphical methods were used to obtain rate constants from equations (4), (5) and (6). The results are given in Table 12. The initial partial pressures are given to indicate the various reactant ratios used. The pressures were considered reliable to 0.2 mm and the temperatures to 0.05 degree. The rate constants in the dimensions $\text{mm}^{-1} \text{ hr}^{-1}$ were obtained from the slopes of the lines drawn through the data points.

The data show a close adherence to the second-order kinetic laws, slight deviations appearing only near the completion of the reaction. An activation energy plot given by the data is shown in Figure 5. The slope of the line corresponds to an activation energy of 17 kcal per mole. Although this is a reasonable value for a homogeneous, bimolecular reaction, the homogeneity of the reaction has not been definitely established experimentally.

Table 12

KINETIC DATA FOR THE REACTION OF FLUORINE AND
BROMINE TRIFLUORIDE IN THE GAS PHASE

Apparatus: Nickel and Monel
Reaction Rate Followed Manometrically

Experiment	Initial Pressure		Temperature (C)	Rate Constant, k (mm ⁻¹ hr ⁻¹)
	F ₂ (mm)	BrF ₃ (mm)		
6-8	103.9	99.8	75.9	1.83 × 10 ⁻³
6-12	49.8	49.8	75.8	1.85 × 10 ⁻³
6-14	99.6	99.4	76.0	1.87 × 10 ⁻³
6-19	592.6	50.0	76.0	1.86 × 10 ⁻³
6-20	591.1	49.9	76.1	1.88 × 10 ⁻³
6-21	562.2	100.0	76.0	1.92 × 10 ⁻³
6-22	304.7	99.5	76.0	1.92 × 10 ⁻³
6-26	98.0	99.4	85.0	3.45 × 10 ⁻³
6-27a	583.5	100.4	85.1	3.51 × 10 ⁻³
6-27b	150.0	149.4	85.1	3.33 × 10 ⁻³
6-28	150.4	150.2	95.0	6.55 × 10 ⁻³
7-5	148.7	149.4	105.5	11.2 × 10 ⁻³
7-6	296.3	99.9	105.5	12.1 × 10 ⁻³
7-10	150.2	149.5	115.7	21.2 × 10 ⁻³

FIGURE 5.

TEMPERATURE DEPENDENCE OF THE GAS PHASE REACTION
BETWEEN FLUORINE AND BROMINE TRIFLUORIDE.

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7. Chemical Equilibria in the Gaseous System Bromine-Bromine
Trifluoride-Bromine Monofluoride
(R. K. Steunenberg, R. C. Vogel, G. W. Redding)

Bromine monofluoride has appeared frequently in various volatilization processes involving bromine trifluoride as a result of the reaction

Equilibrium measurements have been made on this reaction using manometric and spectrophotometric methods. Although portions of these studies had been reported previously (ANL-5494, page 44 and ANL-5529, page 48), the final results have not been summarized.

The experimental procedure consisted of mixing known pressures of gaseous bromine and bromine trifluoride in a vessel of known volume. Since the reaction causes a change in the number of moles of gas present, its extent could be derived from total pressure measurements on the mixture. Similar information was obtained by spectrophotometric examination of the mixtures, which indicated the partial pressures of unreacted bromine and bromine trifluoride in the system.

The apparatus consisted essentially of two nickel vessels, each of about 500 ml volume. One was used as the reaction vessel, the other as a metering vessel. Both were connected to a manifold system with helium and vacuum sources, and a pressure transmitter.⁹ The transmitter permitted the use of a mercury manometer for the pressure measurements. The apparatus, with the exception of the manometer system, was enclosed in a heated air thermostat. Provisions were made so that 10-cm spectrophotometer cells could be attached to the system. The cells were of nickel, with replaceable quartz windows.

Since the quantities of bromine and bromine trifluoride added to the system were based on pressure measurements, it was necessary to determine their vapor densities. Values of 161 g/GMV for bromine (theor. 159.8 g/mole) and 140.5 g/GMV for bromine trifluoride (theor. 136.9 g/mole) were obtained by the Regnault method. These values, although somewhat high, were normal and within the accuracy of the experiments.

For the manometric measurements, the reaction vessel was filled with a known pressure of bromine trifluoride. The desired pressure of bromine was then added to the reaction vessel, as indicated by the pressure drop in the metering vessel. The partial pressures of bromine and bromine trifluoride, a and b, respectively, were calculated from the pressures added and the volume factors. The total pressure of the mixture, P, was measured directly. If x represents the excess pressure produced by

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the reaction, then

$$\begin{aligned}x &= P - (a + b) \\3x &= P_{\text{BrF}} \\a - x &= P_{\text{Br}_2} \\b - x &= P_{\text{BrF}_3}\end{aligned}$$

The equilibrium constant for the reaction, K_p , can then be expressed as

$$K_p = \frac{P_{\text{BrF}}^3}{P_{\text{BrF}_3} P_{\text{BrF}_2}}$$

$$K_p = \frac{(3x)^3}{(a-x)(b-x)}$$

Manometric data obtained by this method gave, over a temperature range from 55 C to 105 C, the following equation when they were subjected to a least-squares treatment:

$$\log_{10} K_p = -\frac{2597.06}{T} + 7.83262$$

K_p is in atmospheres and T in degrees Kelvin.

The spectrophotometric determinations were made in much the same way, except the mixture was expanded into the cell before the total pressure was measured. The partial pressures of bromine, $(a-x)$ and bromine trifluoride, $(b-x)$, were then determined directly from their absorptions at 4170 Å and 2400 Å, respectively. The partial pressure of bromine monofluoride, $3x$, was then given by

$$3x = P - [(a-x) + (b-x)]$$

The spectrophotometric equilibrium constants gave the expression

$$\log_{10} K_p = -\frac{2816.10}{T} + 8.41011$$

Since the spectrophotometric data give the amounts of each reactant consumed, x_a and x_b , it is possible to calculate the ratio of fluorine to bromine atoms in the product:

$$n = \frac{3x_a}{x_a + 2x_b}$$

For all the spectrophotometric determinations the value of n was 0.99 ± 0.12 . The latter figure is the average deviation from the mean.

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Using the temperature-dependence equations for the equilibrium constants, thermodynamic data can be calculated for 298.16 K. This represents a 30-degree extrapolation below the temperature range of the measurements.

At 298.16 K

$$\log_{10} K_{p \text{ atm}} = -0.87767 \text{ (manometric)}$$

$$\log_{10} K_{p \text{ atm}} = -1.03482 \text{ (spectrophotometric)}.$$

From

$$\Delta F = -RT 2.303 \log_{10} K_{p \text{ atm}}$$

$$\Delta F = -1200 \pm 80 \text{ cal/mole (manometric)}$$

$$\Delta F = -1400 \pm 180 \text{ cal/mole (spectrophotometric)}.$$

The slopes of the least squares lines and their standard deviations indicate an enthalpy change for the reaction of

$$\Delta H = 11,900 \pm 500 \text{ cal/mole (manometric)}$$

$$\Delta H = 12,900 \pm 700 \text{ cal/mole (spectrophotometric)}.$$

Using the more accurate manometric data, and taking the gases at 1 atm and 298.16 K as the standard state, the results may be summarized as follows:

$$\Delta H^\circ = 11.9 \pm 0.5 \text{ kcal/mole}$$

$$\Delta F^\circ = -1.2 \pm 0.08 \text{ kcal/mole}.$$

Using these values, it was possible to arrive at the enthalpy and free energy of formation of bromine trifluoride, which were not available previously. Thermodynamic data are available in the literature¹⁰ for the reaction

$$\Delta H^\circ_{298.16} = -18.4 \pm 0.5 \text{ kcal/mole}$$

$$\Delta F^\circ_{298.16} = -18.7 \text{ kcal/mole}.$$

¹⁰ Evans, W. H., Munson, T. R. and Wagman, D. D., J. Research Nat'l. Bureau of Standards, 55, 147 (1955).

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ization were obtained from the data of Oliver and Grisard.¹¹

as follows:

- (3) The enthalpy and free energy of the equilibrium reaction were determined. The standard enthalpy and heat of formation of bromine trifluoride were calculated from these data.

¹¹ Oliver, G. D. and Grisard, J. W., J. Am. Chem. Soc., 74, 2705 (1952).

¹²Brodersen, P. H. and Schumacher, H. J., Z. fur Naturforsch., 2a, 358 (1947).

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B. Pilot Plant Operations

(W. J. Mecham, R. C. Liimatainen, R. W. Kessie, J. I. Thigpen, *
G. E. Goring, ** A. Freeman, W. Pehl, H. Brown, L. Dorsey)

1. Decontamination Run D-6

The current fluoride volatility process pilot plant run is the latest in a series designed to demonstrate the effectiveness of fractional distillation as a method for decontaminating uranium hexafluoride from mixed fission product fluorides. The general procedure, the equipment, and earlier results have been described in previous quarterly reports. The run described herein provides a more stringent criterion of the performance of the volatility method, since a charge was used for about 50 times higher level of activity and only 40 per cent as long cooling time as compared with the previous run. The sequence of process operations is summarized in Table 13. All process operations were performed in the period 79 to 89 days cooling.

Table 13

SEQUENCE OF PROCESS OPERATIONS IN RUN D-6

Step	Description of Operation	Approximate Conditions			
		Temp. C	Press., psia	Reflux Ratio L/D	Time, hr
<u>Operations in Dissolver and Column</u>					
1	Dissolution of slugs	120	40	-	12
2	Re-fluorination with F ₂	50 - 70	55	-	13
3	Column start-up	75	45		12
4	Volatile waste forecut	75	45	high ^a	4
5	UF ₆ rough product cut ^b	85	45	10	20
<u>Operations in Purification Column</u>					
6	Column start-up	85	45		24
7	Volatile forecut 1	90	45	20	6
8	Volatile forecut 2 ^c	-	-	-	-
9	Column start-up	90	45		21
10	UF ₆ product cut	90	45	20	13
11	Column residue collection	-	-	-	1

^aIntermittent take-off.

^bThis fraction was used as charge to the purification column.

^cConsisted of hold-up in column collected as separate fraction.

*Special scientific employee on loan from Hercules Powder Company

**Special scientific employee on loan from Union Carbide Nuclear Company

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a. Dissolution (Step 1, Table 13)

The charge to the dissolver was 13.9 kg of natural uranium metal that had been Hanford-irradiated 211 days and cooled 80 days at the beginning of fractionations (430 g/t). The cladding had been removed prior to charging and slices had been obtained for analytical determinations, the results of which are included in Table 14 (Step 1).

Table 14

ACTIVITIES IN PROCESS FRACTIONS-RUN D-6

All data corrected to 90-day cooling.

The total beta and gamma activities indicated are uncorrected for uranium-237.

Step ^a	Description	Process Fraction		Activity, ct/(min)(gram sample)			
		Amount (lb)	UF ₆ (Weight %)	Total Beta	Total Gamma	Tellurium Beta	Iodine Beta
1	Metal Charge	31.7	-	5.3×10^{10}	4.1×10^{10}	4.6×10^8	1.7×10^7
2	Dissolver ^b Solution after Refluorination	255	27	6.6×10^9	5.1×10^9	5.8×10^7	2.1×10^6
4	Volatile Forecut	2	4	2×10^8	2×10^7	2×10^8	4×10^4
5	UF ₆ Rough Product Cut	66	78	1.2×10^7	1.2×10^6	1.2×10^7	2.8×10^3
7-8	Purification Column Forecut ^c	23.6	60	2.7×10^5	1.4×10^4	1.6×10^5	3.1×10^2
10	Product UF ₆ ^d	21.1	100	5.1×10^4	1.3×10^4	1.6×10^2	32
11	Column and Still Residue ^e	10.2	100	1×10^5	1.1×10^4	3.0×10^3	3.2×10^2

^aSee Table 13

^bCalculated value obtained from initial slug slices dissolved in nitric acid reported in Step 1.

^cComposite of two cuts.

^dUranium-237 activity of uranium irradiated under these conditions but free from fission products at 90-day cooling is about 5×10^4 ct/(min)(gram sample) beta and 1.3×10^4 ct/(min)(gram sample) for gamma.

^eComposite of column holdup and still pot residue.

The dissolution medium, consisting of 186 lb bromine trifluoride and 23 lb uranium hexafluoride, was added at room temperature. Steam was then applied to the dissolver coils to raise the temperature to about 60 C to initiate the reaction, after which heat was removed and material taken overhead to maintain conditions constant at 120 C and 38 psia during the dissolution. A fairly constant high rate of dissolution (with product take-off) continued for 10 hr, and a lower rate (without product take-off, but with noticeable heat evolution) for 4 more hours. A total of 17 hours at 120 C was allowed to insure that the slugs were completely dissolved. No difficulty was encountered with control. The overall penetration rate was about 50 mils/hr, slightly slower than in the previous run.

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After dissolution, the material collected overhead was returned to the dissolver, and the combined solution was slowly sparged with elemental fluorine to regenerate bromine trifluoride from bromine produced during dissolution (Step 2, Table 13).

The decontamination operations consisted of batch fractionations of the re-fluorinated dissolver solution. Boilup rates were 20 to 62 lb/hr in all distillations. Conditions under which these operations were carried out are summarized in Table 13 (Steps 3 through 5 for the dissolver column, and Steps 6 through 11 for the purification column).

The purification column was a 16-foot, 2-inch diameter tower packed with Heli-Pak. After a total reflux start-up period, two forecuts (fractions 7, 8 of Table 14) were taken overhead, serving to remove most of the bromine pentafluoride and tellurium. After another total reflux start-up period, the uranium hexafluoride product cut (fraction 10) was taken overhead. Finally, the entire column residue was collected overhead in two portions (fraction 11).

In spite of the rather high activity level and short cooling time of the slugs charged, a very small amount of fission product activity (other than tellurium) followed the uranium hexafluoride overhead from the dissolver solution. Where high levels of activity appeared (either beta or gamma), they were found to be due to tellurium or to uranium-237. Gamma scans* of liquid samples of product distillate immediately after collection showed no peaks other than uranium-237, except for very slight tellurium peaks.

Figure 1 displays a 2x10 grid of dot patterns representing the digits 0-9. The top row shows digits 0-9, and the bottom row shows digits 0-9. Each digit is formed by a specific arrangement of black dots on a white background.

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To confirm the absence of fission products when the strong uranium-237 peaks were not present, another gamma scan of a product fraction* was made later at a total of 140 days cooling. This scan showed no peaks other than those present in natural uranium. The scan range was 30 to 2000 kev. From the above scans, it is considered that fission products having gammas in the energy region greater than 0.3 Mev are contributing less than one per cent of the gamma activity of aged unirradiated natural uranium. For fission products with energies below 0.3 Mev, there is possible coincidence with the several uranium peaks, but their contribution could not be greater than 10 per cent of the uranium activity. The total activity of this product re-check sample was found to be 7×10^3 beta ct/(min)(g UF₆) and 70 gamma ct/(min)(g UF₆). Pertinent to the ultimate levels of decontamination, it should be noted that the activity of uranium free from fission products has, at 90-day cooling, about 5×10^4 beta ct/(min)(g UF₆) and 1.3×10^4 gamma ct/(min)(g UF₆) due to uranium-237. Also, the activity of aged unirradiated natural uranium is 9×10^4 beta ct/(min)(g UF₆) and 3×10^3 gamma ct/(min)(g UF₆) due to uranium daughters at secular equilibrium.

d. Decontamination Factors

The activities in Table 14 and the decontamination factors presented in Table 15 were all corrected to a common basis of 90-day cooling and corrected for dilution with unirradiated uranium in the dissolution medium.

The gross beta and gamma decontamination factors include the uranium-237 activity and therefore are not true fission product decontamination factors. The individual fission product decontamination factors are based on chemical separations. The total fission product decontamination factor given in Table 15 is calculated as the total activity charged to the dissolver (per gram of total uranium present in the dissolver before distillation) divided by the sum of the activities (per gram of uranium in sample) determined in specific fission product analyses. Justification for this procedure is based on the evidence cited above of the absence of gamma-emitting fission products other than tellurium and iodine and is supported by considerations of the fission yield, half-life, and volatility of fluorides of fission products in general, which limit sources of contamination to tellurium, iodine, antimony, niobium and ruthenium.

*A liquid sample of product UF₆ was taken, then totally distilled before hydrolysis to leave behind nonvolatile uranium daughter activities. Counting was done the same day. Activity growth from uranium-238 decay is about 3 per cent per day.

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Table 15

URANIUM DECONTAMINATION FACTORS^a RUN D-6

All data corrected to 90-day cooling.

Operation	Total Beta ^b	Total Gamma ^b	Tellurium Beta	Iodine Beta	Total Fission Product
Dissolver distillation:					
UF ₆ Rough Product Cut	1.6×10^3	1.3×10^4	14	2.2×10^3	1.6×10^3
Purification distillation:					
UF ₆ Product Cut	3.0×10^2	1.2×10^2	9.6×10^4	1.1×10^2	8×10^4
Overall:					
UF ₆ Product Cut	4.8×10^5	1.5×10^6	1.4×10^6	2.3×10^5	1.3×10^8

^a Decontamination Factor = $\frac{\text{activity per gram uranium hexafluoride in charge}}{\text{activity per gram uranium hexafluoride in product cut}}$

^b Largely U²³⁷ activity.

A good activity balance on iodine was obtained. Substantially all the iodine entering with the slugs was contained in the recovered bromine trifluoride. A separate iodine removal step is considered feasible, but was not carried out in the present operations.

e. Behavior of Niobium, Ruthenium and Plutonium

Determinations of niobium, ruthenium, antimony and plutonium in the process fractions are in progress. Preliminary results indicate that plutonium in any overhead fraction was the order of 10 parts per billion of uranium, and that niobium and ruthenium in all uranium hexafluoride fractions were below 140 gamma ct/(min)(g UF₆). The niobium and ruthenium activities in the recovered bromine trifluoride fraction were 8.8×10^3 and 3.4×10^4 gamma ct/(min)(g BrF₃), respectively. Antimony (Sb¹²⁵) has not been determined quantitatively, but is a minor constituent and apparently offers no difficulties in separation.

f. Bromine Contamination

Bromine contamination of uranium hexafluoride product is being studied. In this run, the product fraction contained about 0.6 wt per cent bromine. Some samples showed as little as 0.01 per cent bromine, but fractionation behavior was not consistent at low bromine levels.

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g. Material Balance

An overall material balance shows about 20 lb of material unaccounted for. This material, mostly uranium hexafluoride, was found in the waste scrubber solution. The loss is attributed to venting operations during column start-up and sampling. It is believed that equipment modifications can eliminate such losses.

2. Distillation Column Runs (C-1 and C-2)

The separation by fractional distillation of uranium hexafluoride from mixtures containing volatile metal fluorides is pertinent to both uranium decontamination from fission products and to uranium purification from impurities commonly found in ore concentrates. The objective of the present column runs C-1 and C-2 was to examine the separation behavior of uranium hexafluoride in a system containing molybdenum and vanadium fluorides, which are likely to be present in uranium ore concentrates. The column* used had a 16-ft, 1.75-inch I.D. tower packed with Heli-Pak 3019. In run C-1, the separation of a uranium hexafluoride-molybdenum hexafluoride mixture at total reflux was measured, and in run C-2 a purified uranium hexafluoride product was collected from a mixture containing both molybdenum and vanadium fluorides.

a. Run C-1

The base charge in Run C-1 was 105.4 lb of a "high purity" uranium hexafluoride.** To this was added 5.71 g molybdenum hexafluoride, which was equivalent to 55 ppm molybdenum. This mixture was held at total reflux for 25.5 hours under the following conditions: pressure, 45 psia; temperature, 90 C; boil-up, 46 lb uranium hexafluoride/hr. The results of samples taken during the run are shown in Table 16. Decreasing values of molybdenum content in the column samples are attributed to withdrawal of material by sampling.

The results indicated that molybdenum hexafluoride is more volatile than uranium hexafluoride in solution and is readily separated by distillation. The separation factor at the end of the total reflux period was about 250. Assuming ideal behavior and using vapor pressure data available

*Referred to previously as "A" column or the "purification column."

**The uranium hexafluoride was obtained from K-25. The specification called for standard production grade material.

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Table 16

DISTRIBUTION OF A MoF₆-UF₆ MIXTURE AT TOTAL REFLUX

<u>Phase of Operation</u>	<u>Stream Sampled</u>	<u>Mo Content, ppm</u>
Still pot charge	Still pot liquid	91
12 hr on total reflux	{ Column overhead vapor Column bottom vapor	9100
24 hr on total reflux	{ Column overhead vapor Column bottom vapor	8700 52
25.5 hr on total reflux	{ Column overhead vapor Column bottom vapor	6500 26

in the literature¹³ for the molybdenum hexafluoride-uranium hexafluoride system, the separation factor of 250 corresponds to an HETP of about 15 inches; this HETP is almost twice that for the bromine pentafluoride-uranium hexafluoride system reported previously. However, the present data are regarded as preliminary approximations pending further checks on sample reproducibility and on the ideality of the system.

b. Run C-2

The material remaining in the column from Run C-1 was used as a base charge to which was added more molybdenum and uranium hexafluorides for the still pot charge in Run C-2. The 37.44 g of molybdenum hexafluoride added was equivalent to 360 ppm molybdenum. The vanadium pentafluoride added was that resulting from the reaction of 2.57 g of vanadium metal and 26.1 g bromine trifluoride; this was equivalent to 54 ppm vanadium and 320 ppm bromine. Conditions of column operation were: pressure, 45 psia; temperature, 90 C; boil-up, 35 lb uranium hexafluoride/hr.

The process operations in run C-2 consisted of two forecuts followed by an overhead product cut. The process steps and corresponding sample determinations are shown in Table 17.

From the results of Table 17, it is evident that both molybdenum hexafluoride and vanadium pentafluoride were concentrated at the top of the column. That is, they were separated as components more

¹³ Ruff, O. and Archer, E., Z. Anorg. Allgem. Chem., 196, 413 (1936).

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Table 17
FRACTIONATION OF A MoF_6 - VF_5 - UF_6 MIXTURE

Process Step	Phase of Operation	Amt in Fraction, lb	Stream Samples	Content, ppm	
				Mo	V
0	Charge	105.4	Still pot liquid	460	31
1	Total reflux (after 24 hr)	-	Overhead vapor	7500	136
			Bottom vapor	260	41
2	Forecut 1 (30/1 reflux ratio)	5.1	Distillate vapor	144	7
3	Forecut 2 (column holdup)	8.2	Distillate liquid	337	45
4	Total reflux (after 24 hr)	-	Overhead vapor	244	42
5	Product Cut (10/1 reflux ratio)	60.4	Product (distillate liquid)	1.4	<1
6	Column residue	4.2	Still pot liquid	~7	~10

volatile than uranium hexafluoride, resulting in a uranium hexafluoride product of high purity. This behavior of vanadium pentafluoride was unexpected because of the sublimation point of 111 C reported in the literature.¹⁴

Of the 105.4 lb uranium hexafluoride charged to the column for runs C-1 and C-2, 78 lb were recovered as column fractions and sample collections. It is believed that the balance of the material will be found in the scrub tower solution, having entered there as a result of purging sample lines and venting the column at start-up. This circumstance is undesirable from a practical viewpoint but does not alter conclusions as to purity of the product fraction actually collected. Of the total molybdenum and vanadium charged, about 8 per cent of each was determined in the uranium hexafluoride fractions collected. The balance is believed to have been lost to the scrub tower in venting, because very high concentrations were present at the top of the column.

c. Sampling and Analysis

Vanadium and molybdenum were determined by colorimetric procedures developed by the Service Analytical Laboratory of this Division. From control determinations, the methods were accurate to better than 10 per cent for samples with values above 1 ppm.

3. Fused Salt Process Equipment

In the present periods, the fused salt process equipment was given shakedown tests. The salt mixture was melted in the makeup tank and charged as liquid to the dissolver. A program of inactive testing is under way.

¹⁴Ruff, O. and Lickfelst, H., Ber 44, 2539 (1911).

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III. FLUIDIZATION

(A. A. Jonke)

Fluidization process studies during this quarter were concentrated primarily on the development of the fluorination process for refining uranium ore concentrates. In addition to experiments with South African Rand ore concentrate, studies were carried out on the preparation of crude green salt from five different types of domestic ore concentrates. Several of these concentrates were found to consist of very fine, non-fluidizable powders. A technique for converting these powders to a fluidizable size by briquetting, crushing, and screening was developed.

Reduction and hydrofluorination experiments showed that the domestic ore concentrates were less reactive than the Rand material, but the degree of conversion to crude green salt obtained is considered adequate for these intermediate process steps. A number of elements present as impurities, such as sulfur, arsenic, boron, molybdenum, and silicon, were partially or completely removed during reduction and hydrofluorination.

Corrosion tests were made during the reduction and hydrofluorination of several of the ore concentrates. These exploratory tests indicated that stainless steel Types 304 and 347 may be satisfactory materials for the reduction operation and Inconel may be suitable for the hydrofluorination step.

Installation of the green salt pilot plant was nearly completed, and initial testing of the "hydraulics" of the system was started, using uranium trioxide as the solid phase and air as the gas phase.

Fabrication of the fluidized-bed calciner for reactor fuel processing wastes was completed and installation of this unit in a shielded cell was started.

Work on the fundamental study of fluidization characteristics of particle mixtures was centered on eliminating the effect of static electricity, which is believed to be the cause of the non-reproducible data obtained. The use of graphite particles in place of glass beads has yielded improved data.

A. Fluorination Process for Refining Uranium Ore Concentrates
(N. Levitz, E. Petkus, J. Thigpen,* M. Jones, T. Cannon)

A tentative flow diagram for the fluorination process for the production of refined uranium hexafluoride was presented in the previous report (ANL-5602, page 56). The process involves reduction and hydrofluorination of uranium ore concentrates, fluorination of the crude green

*Special scientific employee on loan from Hercules Powder Company.

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salt, and fractional distillation of uranium hexafluoride. Work was continued on the development of the fluidized-bed technique for the production of crude green salt from various ore concentrates.

1. South African Rand Ore Concentrates

Previous experiments showed that Rand ore concentrate, after crushing and screening, could be continuously converted to crude uranium tetrafluoride in two single-stage, fluidized-bed reactors, one for reduction and one for hydrofluorination. The reactivity of the Rand concentrate was high, so that greater than 90 per cent conversion was achieved with an overall residence time of about 6 hours for the two steps. Several additional runs with Rand concentrate were made during this quarter to demonstrate the process more fully and to study some of the operating variables.

One additional reduction run was made to determine the effect of increasing the reduction temperature from 575 C used in previous runs to 625 C. The results given in Table 18 show that approximately the same percentage reduction (94.4 per cent average) was achieved in this run as in the previous run (95.8 per cent average) with a residence time of about 3.5 hours in each case. The temperature increase of 50 C resulted, therefore, in no noticeable improvement in reduction. The feed rate for this run corresponded to 40 lb of uranium per hour per square foot of reactor cross section or 23 lb per hour per cubic foot of bed volume.

Since impurities in the sample interfered with the quantitative determination of tetravalent uranium, the percentage reduction was determined by comparing the total reducing power of a sample aliquot with the reducing power of a second aliquot which had been passed through a Jones reductor.

To determine whether the higher reduction temperature had a detrimental effect on the rate of hydrofluorination, the product from the reduction run was continuously hydrofluorinated in the 3-inch, single-stage reactor. During this run (No. 29) difficulties were encountered in maintaining a steady flow of hydrogen fluoride gas from the feed cylinder. This was corrected in the latter portion of the run, after which time the product attained an AOI (ammonium oxalate insoluble) content of about 3.8 per cent in a residence time of 2.8 hours. Comparison with Run 27, which used Rand ore reduced at 575 C and gave a product containing 3.7 per cent AOI in a residence time of 2.2 hours, indicates that the higher reduction temperature had very little effect on the rate of hydrofluorination with this material.

Analysis of the crude uranium tetrafluoride product from this and previous hydrofluorination runs showed that a number of the impurities were reduced in concentration due to the formation of volatile compounds during reduction or hydrofluorination. The analytical results given in

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Table 19 show that sulfur, arsenic, boron, molybdenum, and silicon were largely removed by this treatment, and that phosphorus and vanadium may be somewhat reduced in concentration. Molybdenum and vanadium are of particular interest because these elements form fluorides of intermediate boiling point and are therefore more difficult to separate from uranium hexafluoride by fractional distillation. Any separation of these elements in the hydrofluorination step is therefore advantageous.

Table 18

SUMMARY OF RAND ORE REDUCTION RUN 40

Equipment: 6-inch diameter, stainless steel,
single stage reactor.

Operating Conditions:

Starting Bed:	about 34 lb of reduced ore from Run 39
Static Bed Depth:	about 21 inches
Bed Temperature:	625 C
Gas Composition:	75% H ₂ , 25% N ₂
Gas Velocity:	0.4 ft/sec
Feed Rate:	11.6 lb/hr
Residence Time:	3.5 hr
Duration:	7.6 hr

Run Results

<u>Hours After Start</u>	<u>Percentage Reduction*</u>
1	95.6
2	91.7
3	92.6
4	90.6
5	95.4
6	97.2
7.6	97.4

*By comparing total reducing power with that of second aliquot reduced in a Jones reductor.

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Table 19

CHEMICAL ANALYSIS OF RAND ORE CONCENTRATE BEFORE
AND AFTER REDUCTION AND HYDROFLUORINATION

Element	Analysis	
	Ore Concentrate	Crude UF ₄ (Run 27)
U	68.88%	72.8%
SO ₄	2400 ppm*	830 ppm*
As	400 ppm	<10 ppm
B	10 ppm	<0.1 ppm
Mo	9.6 ppm*	2.0 ppm*
P	50 ppm	<50 ppm
Si	9600 ppm*	<10 ppm
V	<50 ppm	<20 ppm

*Gravimetric or colorimetric analyses; all others are spectrographic except uranium, which is by X-ray fluorescence.

2. Domestic Ore Concentrates

All of the previous experiments on fluidized-bed production of crude uranium tetrafluoride were performed with South African Rand ore concentrate. In order to extend these studies to domestic ore concentrates, five samples of concentrates representing material produced by several major suppliers were obtained. The sources of these concentrates together with the type of process used and the nature of the final product are summarized in Table 20. Chemical analyses of the ore concentrates are listed in Table 21.

These domestic ore concentrates consist primarily of diuranates of sodium or magnesium, depending upon whether sodium hydroxide or magnesium oxide is used as the precipitant. Although ammonium hydroxide is used as the final precipitant at the Uravan and Rifle plants, the product is primarily sodium diuranate, because the sodium ion from the salt roast step enters into the final precipitation reaction. By contrast, the Rand ore concentrate consists primarily of uranium oxides produced by calcination of ammonium diuranate.

The process used for the final drying and calcining of the precipitate differs at the various mills. At the Bluewater plants twin drum dryers are used to produce very thin flakes of product, which disintegrate to powder. At Uravan and Rifle an open hearth-type roaster is used to calcine the precipitate at about 600 C. At Durango the final process step is a salt, sodium carbonate, sawdust fusion, which produces a powdered, black oxide.

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Table 20

SOURCE AND NATURE OF DOMESTIC ORE CONCENTRATES
STUDIED IN FLUIDIZATION EXPERIMENTS

	Concentration Process	Precipitant	Nature of Concentrate
Anaconda Acid Leach Plant Bluewater, New Mexico	Acid leach, ion exchange	MgO	Magnesium Diuranate
Anaconda Carbonate Leach Plant Bluewater, New Mexico	Carbonate leach	NaOH	Sodium Diuranate
Vanadium Corp. of America Durango, Colorado	Salt roast, acid leach, vanadium recovery, fusion	--	Black uranium Oxide
Union Carbide Nuclear Co. Uravan, Colorado	Salt roast, acid leach, ion exchange	NH ₄ OH	Sodium Diuranate and U ₃ O ₈
Union Carbide Nuclear Co. Rifle, Colorado	Salt roast, acid leach	NH ₄ OH	Sodium Diuranate and U ₃ O ₈

Table 21

CHEMICAL ANALYSES OF DOMESTIC ORE CONCENTRATES

Element	Analysis (wt %)				
	Bluewater Acid Leach	Bluewater Carbonate Leach	Durango	Uravan	Rifle
U	72.6	63.2	71.0	64.8	66.0
V ₂ O ₅	0.06	0.95	0.12	3.55	2.88
P ₂ O ₅	0.02	0.14	0.03	3.72 ^a	0.46
Cl, Br, I	0.03	0.05	0.15	0.04	0.02
Mo	0.01	0.01	0.01	0.07	0.03
SO ₄	1.88	0.17	2.25	1.93	7.23
Fe	0.47	0.04	0.74	4.62	0.38
F	0.01	0.01	Trace	0.01	0.05
Na				1.27	4.4
Cu	<0.001	<0.001	0.32	0.05	0.04
Pb	0.004	0.03	0.006	0.01	<0.001
Bi	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Sb	<0.001	<0.001	<0.001	<0.001	<0.001
As	0.001	0.001	0.0005	0.59	0.28
B	5 ppm	2 ppm	1 ppm	140 ppm	120 ppm

^aPO₄ instead of P₂O₅

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Examination of the ore concentrates disclosed that the Bluewater Acid Leach, the Bluewater Carbonate Leach, and the Durango concentrates consisted of extremely fine powders, less than 325 mesh. The Bluewater Acid Leach material, for example, was found by microscopic examination to consist of minute transparent crystals only a few microns in diameter. Attempts to fluidize these finely powdered ores resulted in severe channelling and balling.

The Uravan and Rifle concentrates consisted of coarser material ranging from small lumps to fine powder. These materials could be satisfactorily fluidized after the coarse fraction (+30 mesh) was removed. The coarse fraction could also be converted to a fluidizable powder by crushing in a laboratory size jaw crusher.

a. Agglomeration of Ore Concentrates

In order for the fluidization process to be feasible, it was highly desirable that it be applicable to most or all of the many types of ore concentrates under production. Accordingly, preliminary experiments were conducted to determine if the non-fluidizable Bluewater and Durango concentrates could be agglomerated and converted to a particle size suitable for fluidization.

Using the procedure which had been found successful for pelletizing uranium trioxide powder, an attempt was made to agglomerate the concentrates by making a thick paste with water and allowing this mixture to set. It was found, however, that the ore concentrates did not agglomerate by this method, probably because they consist of diuranates, which do not form hydrates. The addition of about 5 per cent of soluble starch as a binder did produce a moderately hard agglomerate which could be crushed and screened to produce a fluidizable powder. However, later experiments showed that the agglomerated material disintegrated to a very fine powder during the reduction step, apparently as a result of decomposition of the starch binder.

Further tests disclosed that the ore concentrates could be formed into hard pellets by means of a hydraulic pellet press at a pressure of about 15,000 psi. These tests indicated that agglomeration might be achieved on a production scale by the use of a continuous briquetting machine. Arrangements were therefore made with the Komarek-Greaves Company, manufacturers of briquetting equipment, to conduct several tests. Fifty-pound batches of the Bluewater Acid Leach, Bluewater Carbonate Leach, and Durango concentrates were successfully briquetted on a production machine, using the dry powder without binders. The briquettes, which were about the size and shape of an almond, were crushed and screened between 40 and 200 mesh to produce a powder which fluidized satisfactorily. The results of the briquetting tests were sufficiently successful to indicate that this technique should be suitable as a continuous, low-cost method for agglomeration of ore concentrates.

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b. Reduction

A series of batch, fluidized reduction runs was made with the five domestic concentrates in the 6-in. diameter reactor to demonstrate the reduction step and compare the reaction rates. The Bluewater and Durango concentrates were briquetted, crushed, and screened; the Rifle and Uravan concentrates were similarly treated but without briquetting. The runs were made at 575 C for a duration of 4 hours, using hydrogen diluted with 40 to 50 per cent nitrogen.

The results of the five runs listed in Table 22 show that the percentage reduction varied from 82 to 98 per cent, depending upon the type of concentrate. Since all of the reduced products were found to be oxidizable at room temperature in air, and in some cases were pyrophoric, it is possible that partial oxidation of the samples occurred in some cases even though precautions were taken to avoid this.

Table 22

SUMMARY OF BATCH FLUIDIZED REDUCTION RUNS
ON URANIUM ORE CONCENTRATES

Equipment: 6-in. diameter, stainless-steel reactor

Conditions: Temperature: 575 C
Gas Composition: 50 to 60% H₂, 40 to 50% N₂
Gas Velocity: 0.4 to 0.6 ft/sec
Static Bed Depth: 6 to 21 inches
Run Duration: 4 hours

Results:

Run No.	Type Ore Concentrate	Uranium in Feed (%)	Uranium in Product (%)		Percent Reduction
			U IV ^a	U Total ^b	
41	Rifle	66.0	71.6	73.2	98
42	Uravan	64.8	70.8	81.6	87
46	Bluewater Acid Leach	72.6	77.8	84.8	92
47	Bluewater Carbonate Leach	63.2	58.0	70.4	82
48	Durango	71.0	63.7	72.2	88

^aTotal reducing power of product.

^bTotal reducing power after passage through a Jones reductor.

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Most significantly it was found that the concentrates which had been agglomerated by briquetting showed no tendency to disintegrate to fine powder during reduction, and no increase in the proportion of fine particles in the bed was detected at the conclusion of the 4-hour run.

Continuous, single-stage reduction runs in the 6-inch reactor were attempted with the Rifle and Uravan concentrates. The feed for these runs was prepared by crushing and screening the ore through a 30-mesh sieve with no attempt being made to remove the fine particle fraction smaller than 200 mesh. After two hours of operation the run using Rifle concentrate was discontinued due to poor fluidization caused by the presence in the bed of a large percentage of fine particles. These fines caused the bed to form into loose balls about 1/8 inch in diameter which settled to the bottom and remained static. It appears, therefore, that agglomeration by briquetting may be required with this concentrate as well as with Bluewater and Durango materials.

Two continuous runs of 7 hours duration each using the Uravan concentrate were completed without mechanical difficulties. The conditions and results of Run 42-A are summarized in Table 23. The percentage reduction averaged about 90 per cent, as compared to about 95 per cent for Rand ore concentrate under similar conditions, indicating that the Uravan material is somewhat less reactive than the Rand.

The second run (No. 43) with Uravan concentrate was essentially a continuation of Run 42-A using approximately the same operating conditions. Unfortunately the samples from this run were accidentally exposed to air before analysis; however, the primary purpose of this run - to demonstrate mechanical operability - was fulfilled. Fluidization behavior of the Uravan concentrate was satisfactory in both runs.

c. Hydrofluorination

The reduced ore concentrates from the preceding series of reduction runs were hydrofluorinated batchwise in the 3-inch diameter Monel reactor. The purposes of these runs were, first, to determine whether there was a tendency for the particles of concentrate to disintegrate due to attrition or chemical reaction; second, to obtain an indication of the reactivity of these materials toward hydrofluorination; and third, to determine the corrosion resistance of several metals in this medium.

The run conditions and results are summarized in Table 24. In Run 34 with Bluewater Carbonate Leach concentrate, a rapid reaction occurred at the beginning of the run which caused the temperature to rise momentarily to 625 C; at the conclusion of the run a portion of the bed near the bottom was found to be caked. It is believed that the temperature surge resulted from too rapid addition of hydrogen fluoride into the bed of uranium dioxide at the start of the run. This problem is not encountered in continuous operation, since the bed consists of partially converted material.

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Table 23

SUMMARY OF CONTINUOUS FLUIDIZED REDUCTION RUN
ON URAVAN ORE CONCENTRATE

<u>Equipment:</u>	6-inch diameter, stainless steel, single-stage reactor
<u>Operating Conditions:</u>	
Starting Bed:	about 30 lb of batch-reduced concentrate
Static Bed Depth:	about 21 inches
Bed Temperature:	575 C
Gas Composition:	65% H ₂ , 35% N ₂
Gas Velocity:	0.4 ft/sec
Feed Rate:	10.3 lb/hr
Residence Time:	3.5 hr
Duration:	7 hr
Run:	42-A

Run Results:

<u>Hours After Start</u>	<u>U IV (%)^a</u>	<u>Total U (%)^b</u>	<u>Percentage Reduction</u>
1	67.7	81.6	83
2	73.6		90
3	70.9	80.9	87
4	72.0		88
5	73.4		90
6	73.2		90
7	75.6	82.0	93

^aTotal reducing power of product.

^bTotal reducing power after passage through a Jones reductor.

The results of the batch hydrofluorination runs are reported in terms of ammonium oxalate insoluble content (AOI), which represents the unconverted uranium dioxide plus any insoluble impurities. Analyses to determine the percentage of impurities in the AOI are not yet completed, except for the UraVan material where the insoluble impurities amount to about 4 per cent as AOI. The preliminary results in Table 24 indicate that the Rifle, Bluewater Acid Leach, and Bluewater Carbonate Leach concentrates are approximately equal in reactivity, having an AOI of 7 to 12 per cent. The UraVan concentrate (AOI 29 per cent) and Durango concentrate (AOI 32 per cent) appear to be lower in reactivity. Moreover, all the domestic concentrates are less reactive than Rand concentrate, which has an AOI of about 1.4 per cent after similar treatment.

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Table 24

SUMMARY OF BATCH FLUIDIZED HYDROFLUORINATION
RUNS ON DOMESTIC URANIUM ORE CONCENTRATES

Equipment: 3-inch diameter, Monel,
single-stage reactor

Operating Conditions:

Temperature: 450 C
 Gas Composition: 61 to 74% HF, remainder N₂
 Gas Velocity: 0.4 to 0.6 ft/sec
 Static Bed Depth: 12 to 19 inches
 HF/U Mole Ratio: 1.8 to 2.1 x stoichiometric
 Run Duration: 4 hours

Results:

<u>Run No.</u>	<u>Type Ore Concentrate</u>	<u>Ammonium Oxalate Insoluble (%)^a</u>
RF-30	Uravan	29
RF-32	Rifle	11
RF-33	Bluewater Acid Leach	12
RF-34	Bluewater Carbonate Leach	7.2
RF-35	Durango	32

^aAOI represents unconverted UO₂ plug insoluble impurities.

Two continuous hydrofluorination runs made with the reduced Uravan concentrate are summarized in Table 25. Fluidization behavior was good and no operating difficulties were encountered. Both runs were made with a feed rate of about 2 lb/hr and a solids residence time of about 4 hours. Run RF-30 was made with a bed temperature of 450 C and with an excess of hydrogen fluoride of about 80 per cent over the estimated stoichiometric amount required for the uranium and impurities. Results of the run showed the unconverted uranium dioxide to be about 8 per cent and total fluoride content of the product about 24 per cent. Run RF-31 was made with a bed temperature of 550 C and a hydrogen fluoride excess of about 170 per cent over the estimated stoichiometric amount. Results showed the conversion to be less than in the previous run, the unconverted uranium dioxide averaging 32 per cent and the total fluoride 20 per cent.

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Table 25

SUMMARY OF CONTINUOUS FLUIDIZED HYDROFLUORINATION RUNS
ON URAVAN ORE CONCENTRATE

Equipment: 3-inch diameter, Monel, single-stage reactor

Operating Conditions:

Starting Bed: 8.5 lb of batch hydrofluorinated concentrate
 Static Bed Depth: about 16 inches
 Inlet Gas Composition: 92% HF, 8% N₂
 Feed Rate: 2.1 lb/hr
 Residence Time: 4 hr
 Duration: 5.5 hr

	<u>Run RF-30</u>	<u>Run RF-31</u>
Bed Temperature:	450 C	550 C
HF/Feed Ratio:	1.8 x stoichiometric	2.7 x stoichiometric
Gas Velocity:	0.33 ft/sec	0.57 ft/sec

Run Results:

Hours After Start	<u>Unconverted^a</u> <u>UO₂(%)</u>		<u>Total U^b</u> <u>(%)</u>		<u>Reduced^c</u> <u>U(%)</u>		<u>Total</u> <u>Fluoride (%)</u>	
	RF-30	RF-31	RF-30	RF-31	RF-30	RF-31	RF-30	RF-31
1	22	17	59.1	60.2	45	-	24.2	23.0
2	9	38	59.6	60.6	51	52	-	-
3	4	48	60.8	62.6	53	56	25.7	17.3
4	8	41	60.1	62.0	53	55	-	-
5	8	16	59.6	60.7	54	53	23.2	20.9

^a Ammonium oxalate insoluble corrected for insoluble impurities.

^b Determined by X-ray fluorescence.

^c Calculated from reducing power determinations.

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These results are consistent with experience with other types of uranium oxides in which high initial reaction temperatures were found to be detrimental. A multi-stage operation using low initial temperatures and higher final temperatures would probably yield optimum results.

The total fluoride content of the product was considerably in excess of that which can be accounted for as uranium tetrafluoride and uranyl fluoride. The remainder, amounting to 8 to 9 per cent fluoride content, was undoubtedly associated with impurities in the ore concentrate. Since the main purpose of the hydrofluorination step is to minimize the requirement for elemental fluorine in the subsequent fluorination step, the total fluoride content of the crude green salt is the most important criterion for judging the adequacy of the hydrofluorination treatment. Thus, even though the reactivity of the Uravan concentrate is somewhat less than the Rand concentrate, the conversion attained is believed adequate for the intended purpose. Moreover, since the other domestic ore concentrates, except the Durango material, were found in the batch experiments to be more reactive than the Uravan concentrate, no reactivity difficulties are expected with these materials.

Analyses for impurities in these runs have been only partially completed. With the Uravan concentrate the molybdenum content was found to be essentially unchanged after hydrofluorination, the original ore containing 0.07 per cent and the product 0.06 per cent. In the case of the Rifle concentrate, however, the molybdenum was reduced from 0.03 per cent originally to 0.006 per cent after hydrofluorination. The behavior of molybdenum thus appears to be inconsistent and may depend upon the nature of the original molybdenum compound or the degree of reduction achieved in the hydrogen reduction step.

The phosphorus content of the Uravan concentrate, originally 3.7 per cent as phosphate ion, remained virtually unchanged after hydrofluorination.

The effect of the reduction and hydrofluorination treatment on the particle size of the product of the hydrofluorination step is shown in Table 26 by the sieve analyses on the bed material before and after processing. The particle size of the Uravan and Rifle concentrates, which did not require briquetting prior to processing, remained relatively stable throughout the reduction and hydrofluorination runs. The Bluewater Acid and Carbonate Leach concentrates, which were prepared by briquetting, crushing, and screening, showed some tendency to disintegrate during the hydrofluorination step, as evidenced by an increase in the minus 200 mesh fraction from about 2 per cent to as much as 25 per cent. The presence of the fine particles did not, however, have any noticeable effect on fluidization behavior.

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Table 26

EFFECT OF REDUCTION AND HYDROFLUORINATION
ON PARTICLE SIZE OF ORE CONCENTRATE

Type of Ore Concentrate	Process Step	Sieve Analysis (%)			
		+60	+100	+200	-200
Rifle	Before Reduction	42.0	26.9	30.7	0.2
	After Hydrofluorination	46.7	25.7	23.5	4.1
Uravan	Before Reduction	40.2	14.9	14.8	30.3
	After Reduction	39.7	14.4	15.0	30.9
	After Hydrofluorination	43.5	17.7	25.7	13.2
Bluewater Acid Leach	Before Reduction	57.3	18.4	23.5	1.2
	After Reduction	70.3	19.7	8.9	1.1
	After Hydrofluorination	31.5	18.6	32.3	17.4
Bluewater Carbonate Leach	Before Reduction	47.4	24.4	25.5	2.7
	After Hydrofluorination	34.9	16.9	22.7	25.4
Durango	Before Reduction	55.0	22.1	21.9	1.0
	After Hydrofluorination	59.3	24.0	16.0	0.7

Since very little disintegration occurred in the reduction step it is likely that stresses induced by the hydrofluorination reaction rather than mechanical attrition were responsible for the break-up of particles. The Durango concentrate, which also received the briquetting treatment, showed no tendency to disintegrate during processing. Apparently the strength of the briquetted particles varies from one material to another.

d. Corrosion Tests*

The materials of construction normally used for reduction and hydrofluorination of refined uranium compounds may not be suitable for use with the impure concentrates. The presence of sulfur, for example, is known to be detrimental to metals like Monel and nickel. It was decided, therefore, to conduct exploratory corrosion tests during the ore concentrate runs to obtain preliminary indication of the resistivity of several metals.

Each specimen was prepared by wet grinding, degreasing with acetone, and weighing prior to insertion into the reactor with half of the sample in the fluidized bed and half in the gas phase above the bed. The

*Tests conducted and evaluations made by W. Seefeldt and W. Palmer of the Corrosion Group.

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coupons were exposed to the indicated environments for periods of 7 to 25 hours. Upon completion of exposure the coupons were boiled in distilled water to loosen and partially dissolve corrosion products. This was followed by brushing with a soft brush, rubbing with a rubber stopper, washing in water and acetone, and finally weighing.

Evaluations were made visually and by an overall average penetration determined by weight loss. Metallographic examinations were made, but no metallurgical changes were detected. The exposure period was probably too short to detect intergranular or other types of local penetration were they to occur.

The results are shown in Table 27 for the reduction runs and Table 28 for the hydrofluorination runs. Of the metals tested in reduction runs, stainless steel types 304 and 347 appear promising. Inconel appeared satisfactory in all runs except the bed phase of the test with Rand ore. "L" nickel showed high weight loss.

Table 27

RESULTS OF EXPLORATORY CORROSION TESTS
DURING REDUCTION OF ORE CONCENTRATES

Run Number	40	41	42, 43
Ore Concentrate	Rand	Rifle	Uravan
Gas Composition	75% H ₂ 25% N ₂	50% H ₂ 50% N ₂	65% H ₂ 35% N ₂
Temperature, C	625	575	575
Gas Velocity, ft/sec	0.4	0.6	0.4
Exposure, hr	7.6	7	18
Average Penetration, Mils			
<u>Bed Specimens</u>			
S.S. 304	+(a,b)	+(b)	+(b)
Inconel	1.4(d)	+(c)	-
S.S. 347	-	0.02(b)	-
"L" Nickel	-	-	3.1(c)
<u>Gas Phase Specimens</u>			
S.S. 304	+(b)	0.005(b)	+(b)
Inconel	0.02	0.005(c)	-
S.S. 347	-	0.004(b)	-
"L" Nickel	-	-	1.2(c)

^aSpecimens showed slight weight gain.

^bDarkened; all other physical characteristics unchanged.

^cEdges preserved; all physical characteristics unchanged.

^dVery rough surface with appearance of a coating.

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Table 28

RESULTS OF EXPLORATORY CORROSION TESTS DURING
HYDROFLUORINATION OF ORE CONCENTRATES

Bed Temperature: 450 C			
Gas Composition: 70% HF, 30% N ₂			
Gas Velocity: 0.4 ft/sec			
Run Number	28 + 29	30 + 31	32(b)
Ore Concentrate	Rand	Uravan	Rifle
Exposure, hr	25	18	8(b)
Average Penetration, Mils			
<u>Bed Specimens</u>			
Inconel	0.03(c)	+(a,c)	0.10(c)
Monel	1.6(d)	3.5(e)	2.4(d)
"L" Nickel	1.8(e)	3.3(e)	-
Hastelloy "B"	-	0.04(c)	0.07(d)
<u>Gas Phase Specimens</u>			
Inconel	0.42(c)	+(a,c)	0.01(c)
Monel	0.78(d)	0.38(d)	0.29(d)
"L" Nickel	0.81(d)	0.38(d)	-
Hastelloy "B"	-	+(a,c)	+(a,c)

^aSample showed slight weight gain.

^bIncludes four hours exposure during reduction run no. 44 at 575 C.

^cLittle change in physical appearance.

^dSurfaces appeared roughened.

^eSample was somewhat eroded.

Inconel and Hastelloy B appeared promising under hydrofluorination conditions. Monel and "L" showed fairly high weight loss. In all cases except one the attack in the bed phase was higher than in the gas phase.

It should be emphasized that the data reported are not all on an equal time basis, and they must therefore be considered qualitative and not usable for design purposes.

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B. Green Salt Pilot Plant
(N. Levitz, T. Cannon)

The components of the multi-stage, fluidized-bed, green salt pilot plant were received from the fabricator and installation of the equipment has been completed except for the hydrogen fluoride metering system and other details. A description of the pilot plant is given in ANL-5560, page 119. The solids metering and conveying system were tested with uranium trioxide at rates up to 20 lb/hr. The four stages of the reduction reactor were charged with oxide and operated at room temperature for several hours to test the "hydraulics" of the system. Additional testing of this type is planned for both reactors before the thermal insulation is applied.

C. Calcination of Reactor Fuel Processing Wastes
(J. Loeding)

Work on this project during the last quarter again proceeded at a greatly reduced rate due to the press of other commitments. Fabrication of the major equipment components was completed and installation of the reactor and panel boards has been started. Barring unforeseen delays, work on this project should proceed at an accelerated pace during the next quarter.

D. Fundamental Studies
(H. Katz, B. Swanson*)

Experimental studies of particle size distribution in fluidized beds were continued in an effort to find the cause of the poor reproducibility of the data previously reported.

Since it is known that glass is an excellent generator of static electricity and since this effect is greatest in a mixture of different particle sizes, many attempts were made to eliminate or control this variable. During previous experiments, the fluidizing air was passed through a water bubbler in order to increase the conductivity of the gas, but variations in flow rate and temperature resulted in considerable variation in humidity. Therefore, the apparatus was modified so that the flow rate through the bubbler was kept constant, with the excess air being bled off before the rotameter. Also, the water bubbler was replaced by a series of saturated salt solutions kept in a constant temperature bath. The results of these runs indicated that at relative humidities below about 50 per cent the results were extremely sensitive to changes in humidity. As long as the humidity remained constant good reproducibility was obtained, but a variation of as little as 0.5 F in wet bulb temperature shifted the curves significantly. Because of the extremely fine control that would be

*On loan for the summer from Illinois Institute of Technology.

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necessary and the limited applicability of the results, this line of attack was abandoned. It is also significant that at relative humidities above 50 per cent the beads became damp, and very erratic results were obtained. At a relative humidity of 80 per cent, the entire bed clumped together and could not be fluidized.

Many other attempts were made to control the static electricity problem. A commercial destaticizer was applied to the beads, but this made them sticky. Since the conductivity of glass increases with temperature, the whole column was operated in an oil bath maintained at 130 to 150 C, but this also failed to control the static. The use of ultra-violet radiation to ionize the air was attempted, but not enough ionization was obtained to cause any significant effect. Various grounding schemes to conduct static charges away from the column also failed. Finally, the inside wall of the column was platinized, leaving a small vertical observation window uncoated, and the column again was grounded. Although the platinum surface showed little evidence of particle accumulation due to static electricity, the window became so heavily coated that observation was impossible.

Several conclusions were drawn from these experiments. First, control of the amount of static charge accumulation in a fluidized bed is extremely difficult, if not impossible. Even if perfect humidity control were possible, the effect might vary with particle size. Second, the use of humidified air may introduce another variable due to the particles becoming damp and sticking. Finally, although static charges cannot be eliminated, it may be possible to conduct them away as rapidly as they are formed and thus effectively eliminate their effect on the behavior of the bed.

Based on these conclusions, it was decided to abandon glass beads in favor of some more conducting material. Both aluminum and magnesium beads were tried, but they were not satisfactory. Although they seemed to generate less static electricity than glass beads, they were not sufficiently conducting due to the formation of an oxide coating. The only material found so far which appears to have suitable properties is graphite. Particles of graphite were fluidized in a grounded copper column, using humidified air. Although the lack of visibility complicated the sampling procedure, good reproducibility was obtained. More recently a grounded Lucite column coated with graphite, except for a small vertical observation window, was used and gave the same results as the copper column. It also appears that with this system humid and dry air give the same results. Although not enough data have been taken to draw any definite conclusions, this system is the most promising that has been tried to date, and work on it will be continued.

IV. REACTOR CHEMISTRY

A. The Yield of Cesium-137 in Fast Neutron Fission of Uranium-235 and Plutonium-239

(P. Kafalas, C. E. Crouthamel, M. Laug, R. R. Heinrich, G. Seto)

The absolute fission yield of cesium-137 has been determined for fast neutron fission of uranium-235 and plutonium-239 by absolute counting of the fission fragments. The cesium-137 activity was determined by absolute counting with an end-window proportional counter. The yields were found to be 6.87 per cent and 7.45 per cent for uranium-235 and plutonium-239, respectively. These values are based on a cesium-137 half-life of 32.6 years.

The fast neutron bombardment and fission counting procedure have been described in a previous quarterly report (ANL-5529, pages 108-120). The fission counting data were corrected for shadowing of the light sample by the heavy sample. This correction was determined by placing thin copper foils on each face of the heavy sample disc and beneath the light sample disc. The 12.8-hr copper-64 activity was assayed with a scintillation counter in order to determine the neutron exposure at the positions of the three copper foils. The correction in each case amounted to 3 to 4 per cent.

The cesium-137 activity was assayed about eight months after the bombardment. This delay ensured that cesium-136 activity was far below the detectable range. Since the burn-up was very low, cesium-134 build-up was negligible. After addition of cesium carrier to the heavy sample solution, the cesium was separated as cesium perchlorate; this was then dissolved and the solution was scavenged three times by ferric hydroxide precipitation. Cesium perchlorate was again precipitated and mounted on glass fiber filter paper for counting.

The plutonium solutions were passed through a cation exchange column (Dowex-50 of 100-200 mesh). The resin was first treated with 2 M hydrochloric acid. The cesium was eluted with 2 M hydrochloric acid and this solution was then treated as described above to separate cesium as cesium perchlorate.

A solution of carrier-free cesium-137 was assayed with a 4π β counter. This solution was then used to calibrate the end-window proportional counter for this particular nuclide. The counting efficiency was determined as a function of the weight of cesium perchlorate per unit area. Using this efficiency factor, the counting rate of the cesium-137 samples was converted to absolute disintegration rate.

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Two uranium samples and five plutonium samples were bombarded. The plutonium samples were of two different isotopic contents, one of low plutonium-240 content (labeled L.A.) and one of about 5 per cent plutonium-240 (labeled R.F.). The results of the fission yield determinations are shown in Table 29 for uranium-235 and in Table 30 for plutonium-239.

Table 29

YIELD OF CESIUM-137 IN FAST NEUTRON
FISSION OF URANIUM-235

Sample No.	Aliquot No.	Total Zero Time Cs ¹³⁷ Activity (dpm)	Number of Cs ¹³⁷ Atoms*	Number of Fissions	Fission Yield (%)
U-10 M	1A	42,810	1.059×10^{12}	15.39×10^{12}	6.88
	1B	42,740	1.057×10^{12}	15.39×10^{12}	6.86
	2A	42,510	1.052×10^{12}	15.39×10^{12}	6.84
	2B	42,310	1.047×10^{12}	15.39×10^{12}	6.80
	3A	41,570	1.028×10^{12}	15.39×10^{12}	6.68
	Average				6.81
U-10	1A	39,340	0.973×10^{12}	14.03×10^{12}	6.94
	1B	39,820	0.985×10^{12}	14.03×10^{12}	7.02
	2A	39,120	0.968×10^{12}	14.03×10^{12}	6.90
	2B	39,850	0.986×10^{12}	14.03×10^{12}	7.03
	2C	39,030	0.966×10^{12}	14.03×10^{12}	6.89
	3A	38,560	0.954×10^{12}	14.03×10^{12}	6.80
	3B	39,460	0.976×10^{12}	14.03×10^{12}	6.96
Average					6.93

Over-all Average Yield = $6.87 \pm 0.17\%$

*The number of atoms was calculated on the basis of Cs¹³⁷ half-life = 32.6 years

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Table 30

YIELD OF CESIUM-137 IN FAST NEUTRON
FISSION OF PLUTONIUM-239

Sample No.	Aliquot No.	Total Zero Time Cs ¹³⁷ Activity (dpm)	Number of Cs ¹³⁷ Atoms*	Number of Fissions	Fission Yield (%)
RF-Pu-3	1	39,170	0.9691×10^{12}	12.62×10^{12}	7.68
	2	37,990	0.9399×10^{12}	12.62×10^{12}	7.45
	3	38,560	0.9540×10^{12}	12.62×10^{12}	7.56
	4-A	38,800	0.9599×10^{12}	12.62×10^{12}	7.61
	4-B	38,180	0.9446×10^{12}	12.62×10^{12}	7.49
Average					7.56
RF-Pu-4	2	31,220	0.7724×10^{12}	10.605×10^{12}	7.28
	4	31,280	0.7739×10^{12}	10.605×10^{12}	7.30
Average					7.29
RF-Pu-5	1	38,340	0.9485×10^{12}	13.04×10^{12}	7.27
	2	38,360	0.9490×10^{12}	13.04×10^{12}	7.28
Average					7.275
LA-Pu-C	1	36,810	0.9107×10^{12}	12.17×10^{12}	7.48
	2	37,180	0.9198×10^{12}	12.17×10^{12}	7.56
	3	36,670	0.9072×10^{12}	12.17×10^{12}	7.45
	4	36,890	0.9127×10^{12}	12.17×10^{12}	7.50
Average					7.50
LA-Pu-E	1	34,360	0.8501×10^{12}	11.46×10^{12}	7.42
	2	34,980	0.8654×10^{12}	11.46×10^{12}	7.55
	3	34,490	0.8533×10^{12}	11.46×10^{12}	7.45
	4	34,280	0.8481×10^{12}	11.46×10^{12}	7.40
Average					7.45

Over-all Average Yield = $7.45 \pm 0.17\%$

*The number of atoms was calculated on the basis of Cs¹³⁷ half-life = 32.6 years.

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These yields are higher than the yields for thermal neutron fission of these nuclides. The best value¹⁵ for thermal neutron fission of uranium-235 is 5.94 per cent. The literature values for the case of plutonium-239 (thermal) vary considerably, but they are all lower than our value of 7.45 per cent. The differences between our values and the literature values are attributed to the differences in neutron energy. Our spectrum is essentially a fission neutron spectrum with some of the lower energy neutrons removed by the boron carbide blanket.

B. Determination of Alpha, The Ratio of Capture to Fission Cross Sections, in EBR-1

(P. Kafalas, M. Levenson, C. M. Stevens*, D. C. Stupegia, M. Homa, G. McCloud, F. Ferry)

Samples of uranium-235, plutonium-239 and uranium-238 have been exposed in various parts of EBR-1 in order to determine the variation of alpha, the ratio of capture to fission cross sections, with reactor position. These samples were exposed during the second loading of EBR-1. The uranium-235 and the plutonium-239 samples have been analyzed radiochemically to determine the burn-up, i.e., the fraction fissioned, and mass spectrometrically to determine the fraction which has undergone the capture process. In the case of uranium-238 the capture events are being determined radiochemically. The uranium-238 samples have not been completely analyzed yet. These results will be reported at a later date.

The samples were sealed in aluminum capsules which were in turn sealed in small stainless steel cylinders. These cylinders were placed in the fuel rods, in the inner blanket rods, and in a brick of the outer blanket. The arrangement of the samples is shown in Figure 6, which is a schematic side-view diagram of EBR-1. The samples were arranged so as to show the horizontal variation of alpha along a radius in the midplane of the reactor and the vertical variation along a rod near the reactor center.

1. Experimental Procedure

The number of fissions per unit weight of sample was determined by measuring the absolute disintegration rate of cesium-137 with a calibrated end-window proportional counter. The chemical separation of cesium as the perchlorate has been described in the preceding section of this report. The cesium-137 activity was converted to the equivalent

¹⁵Steinberg, E. P., and Glendenin, L. E., "Survey of Radiochemical Studies of Fission Process," Proc. of the Int. Conf. on the Peaceful Uses of Atomic Energy, Vol. 7, p. 3 (United Nations, N. Y., 1956)

*Special Materials Division, responsible for mass spectrometric analysis.

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FIGURE 6

SIDE VIEW OF EBR-1 (Schematic) SHOWING SAMPLE POSITIONS
 Numbers in circles refer to sample numbers

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number of fissions by means of fission yields determined in our laboratory for fast neutron fission of uranium-235 and plutonium-239 (see Tables 29 and 30 of this report).

The uranium analyses were performed by X-ray fluorescence measurement. The plutonium analyses were performed by alpha counting of thin samples in a 2π geometry alpha counter.

The ratios of U^{236}/U^{235} and of Pu^{240}/Pu^{239} were determined by mass spectrometry.

2. Discussion of Results

The variation of alpha in uranium-235 along a horizontal radius at the reactor midplane is shown in Figure 7. The line is drawn from the smooth curve values of the number of capture and fission events shown in Figure 8. There is some question as to whether the points in the three regions should all be connected together, or whether they should lie on three discontinuous curves. There is a steel separator of about one-quarter inch between the core and inner blanket. There is a gap of nearly an inch between the inner and outer blanket; in this gap there is a heavy metal wall and an air space. The effect of these gaps on the neutron flux and the neutron energy spectrum may be appreciable. However, since nearly all the points fall on continuous smooth curves, we have assumed that the effect of the gaps is not great.

In Figure 8 the point at 2.55 inches on the fission curve appears low. Several of the aluminum capsules showed signs of having been overheated and partially melted during this exposure. This poor treatment of some of the samples probably is the reason for this apparently erroneous result.

Figure 9 shows the variations of alpha of uranium-235 along a vertical rod (hole No. 5). An oblique point (point No. 8) is also shown in this figure. One point at +11 inches has not been determined yet. The vertical variations in the number of capture and fission events are shown in Figure 10. In Figures 9 and 10, the points are shown connected by lines; these lines are shown merely to tie the points together and are not intended to imply that intermediate points would lie on the lines as drawn here.

Figures 11, 12, 13 and 14 show a similar survey of alpha of plutonium-239. A few points remain to be determined. The comments given above for the uranium-235 curves apply also to the plutonium-239 curves. In Figure 12 the points on the fission curve at 2.55 inches and at 13 inches are probably low due to the causes mentioned above. The points

FIGURE 7
HORIZONTAL VARIATION
OF α OF U^{235} AT MIDPLANE OF EBR-1

FIGURE 8
HORIZONTAL FISSION AND CAPTURE
PATTERNS OF U^{235} AT MIDPLANE OF EBR-1

FIGURE 9

VERTICAL VARIATION OF α OF U^{235} IN EBR-1
(See Figure 6 for sample orientation)

FIGURE 10

VERTICAL FISSION AND CAPTURE PATTERN OF U^{235} IN EBR-1
(See Figure 6 for sample orientation)

FIGURE 11

HORIZONTAL VARIATION OF α
OF Pu^{239} AT MIDPLANE OF EBR-1

FIGURE 12

HORIZONTAL FISSION AND CAPTURE
PATTERNS OF Pu^{239} AT MIDPLANE OF EBR-1

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FIGURE 13

VERTICAL VARIATION OF α OF Pu^{239} IN EBR-1
(See Figure 6 for sample orientation)

FIGURE 14

VERTICAL FISSION AND CAPTURE PATTERNS OF Pu^{239} IN EBR-1
(See Figure 6 for sample orientation)

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at 6.88 inches are low on the capture and fission curves of both uranium-235 and plutonium-239. This fact suggests that the neutron exposure of this set of capsules was less than that of the other capsules.

According to Figure 13, the alpha of plutonium in the upper blanket is smaller than in the core. In the case of uranium-235, alpha is lowest in the core (see Figure 9), where the average neutron energy might be expected to be greatest. Alpha at the vertical point 11 inches above the reactor center has not been determined yet because the mass spectrometric measurements have not been made for either uranium-235 or plutonium-239.

Figure 15 shows the horizontal variation of $(\sigma_f \text{ of Pu}^{239})/(\sigma_f \text{ of U}^{235})$. Figure 16 shows the vertical variation of this ratio. In Figure 15 the ratio rises near the outer edge of the outer blanket to a value which is greater than the thermal value. This rise may be due to the fission resonance in Pu²³⁹ at 0.3 ev, where the fission cross section is 3400 barns. This curve may be compared with Figure 5 of Kaufmann, Kirn, and Loewenstein.¹⁶ The unusual shape of the curve in Figure 16 is not easy to explain.

The horizontal variations of alpha may be correlated with a study of the horizontal variation in neutron energy spectrum determined by Egger, Huddleston, Krohn, and Ringo (to be published in "Nuclear Science and Engineering"). The vertical variation in neutron energy spectrum has not been determined experimentally.

C. Metal Oxidation and Ignition

(H. A. Porte, J. G. Schnitzlein, R. C. Vogel, D. Fischer, F. Mertes*, A. Porter)

The increasing use of uranium, thorium, zirconium and plutonium makes imperative an understanding of the factors which influence their pyrophoric nature. To elucidate these factors a study has been started on the oxidation characteristics of these metals. The reasoning behind the experimental approach for this program has been outlined in ANL-5494, pages 104 to 109. It is felt that conditions which accelerate the oxidation will lower the ignition temperature and increase the possibility of spontaneous ignitions. Thus, an understanding of the kinetics of oxidation and the mechanism of the reaction should help predict when these metals will be unusually sensitive to spontaneous ignition.

¹⁶Kaufmann, S. G., Kirn, F. S., and Loewenstein, W. B. Nuclear Science and Engineering, 1, 193 (1956).

*F. Mertes is a cooperating institution student from Northwestern University with the group summer quarter.

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FIGURE 15

HORIZONTAL VARIATION OF THE RATIO σ_f OF Pu^{239}/σ_f OF U^{235} IN EBR-1
(Taken from smooth curves of Figure 8 and Figure 12)

FIGURE 16

VERTICAL VARIATION OF THE RATIO σ_f OF Pu^{239}/σ_f OF U^{235} IN EBR-1.
(Taken from points of Figure 10 and Figure 14)

During the past quarter this program has been discussed with R. D. Schultz of Aerojet, Richard Smith of Safety and Fire Protection Branch, AEC, D. Krucoff of Reactor Development Division, AEC and J. J. Downing of Technical Operations.

1. Uranium

Work has proceeded toward establishing a set of base-line data in order to appraise critically the influence of specific variables on the pyrophoricity of uranium metal. The apparatus used, the metallurgy of the uranium, the effect of surface preparation, and the effect of temperature on reaction rates are reported in ANL-5602, pages 65 to 77.

Under all conditions studied (see ANL-5602, pages 71 to 77) the oxidation has been found to take place in two stages. The first stage is a slow oxidation. For example, the first stage at 200 C and 200 mm appears to have a rate of about $0.6 \mu\text{gm}/\text{cm}^2$ for a period of about 80 minutes, or until the oxygen consumed was about $50 \mu\text{gm}/\text{cm}^2$. Then the rate accelerates, and in the second stage the rate is constant at about $5.8 \mu\text{gm}/\text{cm}^2\text{-min}$. Both rates were found to be, of course, functions of temperature.

During the past quarter additional runs have been made to clarify the temperature effect. The pressure dependence of the reaction has also been investigated. Equipment has also been ordered for the direct observation of ignition temperatures of compact metal samples and observing the break in the sample temperature at a uniform rate of heating.¹⁷

a. Pressure Dependence

K. T. Perkins¹⁸ has shown a slight pressure dependence on the oxidation rate of uranium at 260 C and an oxygen pressure range from 90 to 370 mm. We have completed a series of runs at 125, 150, 200 and 250 C and a pressure range from 20 to 800 mm.

Comparison of the linear rates (second stage) in Table 31 at 125 C and 150 C show essentially no pressure dependence; that is, the rate is constant within the average deviation from the mean while the pressure was changed 40-fold.

At 200 C a definite dependence of the rate on oxygen pressure is shown in Figure 17. The data at 200 C may be expressed as

$$\text{Rate} = KP^{0.2}$$

¹⁷Fassel, W. M., et al, J. Metals 3, 522 (1951).

¹⁸Perkins, K. T., Oxidation Rates of Tuballoy (U) Metal, CT-1008 (October 1943).

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Table 31

RATES OF OXYGEN CONSUMPTION BY URANIUM AT VARIOUS
TEMPERATURES AND PRESSURES DURING THE
SECOND STAGE (LINEAR RATE)

Rates are reported as average $\pm$ the average deviation from the mean for the tabulated conditions.

Pressure, mm	$\mu \text{ gm/cm}^2 \text{ min}$		
	Temp., C		
	125	150	200
20	0.11 ^a	0.48 $\pm$ 0.06	3.7 $\pm$ 0.6
50	0.12 ^a	0.59 $\pm$ 0	5.24 $\pm$ 0.07
200	0.08 ^a	0.55 $\pm$ 0.02	6.7 $\pm$ 0.6
800	-	0.6 $\pm$ 0.1	8.2 $\pm$ 0.5
Avg	0.10 $\pm$ 0.02	0.55 $\pm$ 0.05	-

^aOnly one run each condition.

FIGURE 17

PRESSURE DEPENDENCE OF SECOND STAGE OXIDATION OF
URANIUM AT 200 AND 250 C IN OXYGEN

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At 250 C the second stage rate goes through a maximum, so quantitative treatment is probably not justified. However, if the maximum rates are considered similarly (see Figure 17), the value of the exponent obtained is 0.3.

Additional critical consideration of the first stage data is necessary before a proper method of presentation can be selected.

b. Electron Micrography

A possible explanation of the change of oxidation from the protective film first stage to the linear second stage would be cracking of the oxide. Although no evidence is observed with usual microscopic techniques, the possibility of submicroscopic cracks needed examination. In order to use electron micrography a technique of replication of the surface had to be found and proved satisfactory.

Maintaining the reservation of as yet incomplete proof of true replication of the surface, four pictures are presented to show the power of such a tool.

The technique for production of carbon-evaporated replicates and their removal from the surface of uranium cubes has been developed by A. Porter, Tom Minick* and L. Roth.* The carbon is evaporated from an arc in an evacuated bell jar with the sample placed a few inches away so that the surface to be examined is at approximately a 30-degree angle. The thickness of the film deposited may be controlled by time and the arc current, i.e., temperature. The replicate is removed from the metal by dipping in nitric acid until it has loosened and then floating the replicate on the surface of distilled water. The replicate is then dipped from the water with the electron microscope support grid. These may be then viewed by electron transmission and appropriate photographs taken.

Carbon replicas can also be prepared by evaporating carbon at an angle of 90 degrees. Such replicas lack contrast. To increase contrast the technique of palladium shadowing may be used. This consists of evaporating palladium from a tungsten filament obliquely onto the sample side of the carbon replica after the removal of the latter.

Electron micrographs of the replicates have been obtained for electropolished (Figure 18), 6-micron diamond paste polished (Figure 19), and electroetched uranium surfaces (Figure 20). It must be emphasized that these represent a technique still being developed and tested. However, Figure 18 demonstrates clearly that the surfaces whose oxidation kinetics

*Electron Microscope Section of the Biological and Medical Research Division, Argonne National Laboratory.

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FIGURE 18

CARBON REPLICA OF ELECTROPOLISHED URANIUM SURFACE

This view is the roughest observed on the electropolished surface.

31,000 X

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FIGURE 19

CARBON REPLICA OF 6-MICRON DIAMOND-PASTE
POLISHED URANIUM SURFACE

This type of polish was used to obtain a comparison with the apparent smoothness of the electropolished surface (Figure 18).

31,000 X

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FIGURE 20

CARBON REPLICA (PALLADIUM SHADOWED) OF AN
ELECTROETCHED URANIUM SURFACE

8,000 X

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are being studied are exceedingly smooth. Figure 19, the replication of a surface "scratched" with 6 μ diamond paste, shows that replication is taking place. Figure 20, replication of electroetched uranium surfaces, shows what may be grain structure.

c. Inconel Contact During Oxidation

Oxidations conducted at temperatures over 300 C cause the sample to attain a temperature higher than the furnace. Using a glass thermocouple well in contact with the sample (ANL-5602, page 66, Figure 19) therefore may cause considerable error in the true sample temperatures for the higher rates. The obvious solution of inserting an Inconel-constantan needle thermocouple (Inconel hypodermic tube with constantan wire inside fused at the tip) into a hole in the cube would introduce the questions of coupling metal and the method of drilling the hole influencing the rate of oxidation.

Samples were prepared by both a high speed, fast cut drill and with the "Elox" apparatus. "Elox" apparatus removes metal by ionization or spark erosion therefore causing less cold work of the metal. The data presented in Table 32 show essentially that no change of second stage rate is caused by "Elox" drilling or the Inconel couple. The direct insertion of the thermocouple thus provides therefore a method of measuring the actual temperature of the cube in high rate runs where it tends to heat because of the heat of reaction.

d. Metallurgical Variables

Work has begun on the study of the effect of certain metallurgical variables on the rate of oxidations. Heat treatments, such as cast, alpha anneal, beta quench and gamma quench, working (as rolled), grain size and randomization, are the first variables being investigated.

2. Zirconium

It was decided that an apparatus similar to that used in the study of the oxidation of uranium would also be appropriate for investigating the oxidation of zirconium. Therefore, construction of the required apparatus has been initiated. In the meantime, the necessary arrangements are being made to procure a number of binary zirconium alloys.

The initial runs will be on pure zirconium at various temperatures and pressures. These will serve to establish a base line to which the rates of oxidation of binary zirconium alloys will be compared.

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Table 32

COMPARISON OF RATES WITH DRILLED CUBES
AND INCONEL COUPLES

Oxidation at 200 C in 200 mm O₂

Cube	Condition	Second Stage
		Linear Rate $\mu\text{gm}/\text{cm}^2\text{-min}$
25	Before drilling	5.7
25E	"Elox" hole ^a	6.6
25EI	"Elox" hole; Inconel couple	6.2
30E	"Elox" hole	6.4
30EI	"Elox" hole; Inconel couple	7.2
29D	Drilled hole ^b	5.4
29DI	Drilled hole; Inconel couple	7.1
Previously established average ^c		6.0 $\pm$ 0.5

^a"Elox" apparatus uses an electrical discharge to remove metal.

^bDrilled with high speed, fast cutting drill.

^cData reported in ANL-5602, page 74, Table 25 have been adjusted to include a few additional more recent runs.

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V. CHEMICAL-METALLURGICAL SEPARATION PROCESSES

The activation energy for the attack of liquid uranium on high purity, high density alumina is 48.2 ± 0.6 kcal/mole. The rate of attack on thorium or beryllia increases with exposure. The acceleration or deceleration of the attack on various crucible materials by the addition of alloying elements to uranium may be understood in terms of wetting behavior, preferential oxidation of solute, and formation of protective films.

Two new phases have been observed in the lanthana-beryllia system.

The extraction of plutonium from hydride-produced 1% plutonium-uranium powder by molten magnesium has been shown to proceed with good efficiency.

Data have been obtained for the partition of ruthenium between liquid magnesium and liquid uranium-iron alloy. The distribution is highly in favor of the heavy metal phase and shows significant variations with temperature and concentration.

Testing of pilot plant equipment components was continued. Analyses of small protrusions ($5/32$ inch in diameter by $3/8$ inch long) cast on poured ingots were in agreement with analyses of the melt and indicate protrusion casting to be a feasible sampling procedure. Two-kilogram charges of sodium-coated uranium pins ($1/8$ inch OD), which simulate discharged fuel material, were satisfactorily melted.

Work has been started on the purification of uranium from noble fission products by fractional crystallization from a solvent metal such as zinc.

Four successive magnesium extractions of plutonium from a uranium-chromium-plutonium alloy (5 w/o chromium, 1 w/o plutonium) resulted in the extraction of 85 per cent of the plutonium. The over-all plutonium material balance was 96 per cent. A five-kilogram scale batch extraction unit has been installed and preliminary testing begun.

Oxidation of sodium-coated uranium pins at 600 C in a 1000 ppm oxygen in argon atmosphere was found to be excessive. Consequently, the oxygen impurity concentration in the cell atmosphere must be maintained at a considerably lower concentration (~ 20 ppm) than 1000 ppm. This represents a considerably more stringent oxygen specification than had been contemplated.

REF ID: A64111

Studies of inert gas purification show that oxygen may be completely removed from argon by reaction with hydrogen previously sorbed on a 0.5 per cent palladium on alumina catalyst. The amount of hydrogen which may be put on the catalyst for subsequent reaction with oxygen is 0.47 ml per ml of catalyst. The use of hot copper was demonstrated to be a satisfactory oxygen gettering method. Although nitrogen removal from the cell atmosphere by chemical means may not be necessary, it was shown that the use of hot calcium at 600 C or sodium-activated calcium at 440 C is effective.

Discussions were held with representatives of American Smelting and Refining, Union Carbide and Carbon and Hanford Operations.

A. Laboratory Studies
(H. M. Feder)

1. Control of Dross in Melt Refining
(N. Chellew, C. Cushing, J. Schilb, D. Finucane)
 - a. Kinetics of Uranium-Ceramic Oxide Reactions
 1. High Purity Uranium

The kinetic study of the alumina-uranium reaction was terminated after data from five new experimental runs were collected. The standard conditions described in ANL-5602, page 92, were used. Of the total number of twenty-five melts made in this study three were in the lowest temperature range, 1140 to 1145 C. In the treatment of the data these three experiments have not been further considered because of difficulties experienced in accurate temperature control and the inadequacy of their number. The remainder of the results of the kinetic studies is shown in Figure 21. The best straight lines representing the data were obtained by a least squares treatment after elimination of two short duration runs in which gross contamination by aluminum is suspected.

The equations for these lines, $W = a + bt$, where W is the amount of aluminum dissolved in milligrams per square centimeter of wetted wall area, and t is the time in minutes, have the following values for a and b :

<u>t, C</u>	<u>a</u>	<u>b</u>
1200	1.704	0.0282
1260	3.400	0.0475
1330	3.656	0.1173

The activation energy for the linear portion of the reaction may be calculated from the slopes of these lines in the usual way. The result is approximately 48 kcal/mole. However, this result was suspect because no

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FIGURE 21

CORROSION OF ALUMINA BY MOLTEN URANIUM

Crucible: Morgan Triangle RR Recrystallized Alumina

Charge: Uranium Containing 20 ppm Carbon, 5 ppm Nitrogen, 11 ppm Oxygen, and 33 ppm Aluminum (Maximum concentrations)

correction was made for reaction occurring during the non-isothermal portions of each run. The influence of these non-isothermal portions, from five to fifteen minutes in length, becomes negligible for runs of very long duration, so the following technique was applied. The extent of reaction was calculated from the equations given for various selected total run durations. For each period of time the apparent activation energy (which now includes the initial reaction as well as the non-isothermal period) was determined from an Arrhenius plot. These apparent activation energies are shown in Figure 22, from which the asymptotic value for the activation energy, 48.2 kcal/mole, may be deduced. The standard error of this value is estimated to be 0.6 kcal/mole.

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FIGURE 22

APPARENT ENERGY OF ACTIVATION vs. TOTAL MELT TIME
 U - Al₂O₃ Kinetic Studies

A study of the reaction of container material with liquid uranium has been initiated using thoria, thoria-coated alumina, beryllia and magnesia crucibles. The crucibles used were fabricated of high purity material and were relatively fine-grained. Melt temperatures were taken by optical pyrometer and corrected to previously determined thermocouple values. Table 33 is a summary of the experiments for which analytical data are available. The results from previous kinetic studies in recrystallized alumina are included for comparison. Nine melts have been made with high purity uranium in lime-stabilized zirconia crucibles at temperatures of 1200, 1260 and 1325 C and melt times of 60, 150 and 240 minutes. Analytical information is not available for these runs except for one order of magnitude result, shown in Table 33.

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Table 33

CONTAMINATION OF HIGH PURITY URANIUM
BY CRUCIBLE MATERIALS

Charge: Maximum uranium impurities - 39 ppm carbon,
5 ppm nitrogen, 11 ppm oxygen.

Conditions: Helium atmosphere. Uranium charges liquated in crucible.

Run	Crucible	Melt Conditions		Contamination ^a	
		Nominal Temp, C	Total Time, min	Element	$\mu\text{g}(\text{cm}^2$ Wetted Area)(hr)
Corrosion Series	Al ₂ O ₃ (recrystallized)	1200		Al	1690
ANL-5602,		1260		Al	2850
Table 34		1330		Al	6850
83E	ThO ₂ (Slip Cast)	1200	120	Th	< 5
87E	ThO ₂ -Coated Al ₂ O ₃	1205	120	{ Al Th	890 < 5
103E	ThO ₂ -Coated Al ₂ O ₃	1300	60	Th	< 10
105E	ThO ₂ -Coated Al ₂ O ₃	1306	152	Th	10
102E	ThO ₂ -Coated Al ₂ O ₃	1300	241	Th	15
86E	BeO (Slip Cast)	1200	120	Be	7
107E	BeO (Slip Cast)	1330	62	Be	17
106E	BeO (Slip Cast)	1330	152	Be	25
108E	BeO (Slip Cast)	1330	242	Be	33
84E	MgO (Dry Press)	1200	120	Mg	nil
85E	MgO (Slip Cast)	1200	120	Mg	nil
92E	ZrO ₂ (CaO Stabilized - Slip Cast)	1200	120	Zr	100

^aAnalytical precision (relative): Al, $\pm 5\%$; Be and Th, $\pm 10\%$;
Zr, order of magnitude;
Mg, spectrographic determination

The contamination of uranium by thorium or beryllium at 1200 C was found to be near the lower limits of analytical determination, hence, a higher temperature was chosen for the rate study. For both elements the preliminary data of Table 33 show the rate increasing with time at least up to four hours. Such behavior, if confirmed by further experiments, can be understood in terms of a two-step mechanism in which the

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first step is zero-order and the second step is first order in metal concentration. For the reduction of thorium the mechanism based on earlier evidence and presented in ANL-5602, page 105, is in accord with these observations; that is,

It is of some interest to note that the porosity of the thorium coat applied on alumina crucible by the manufacturer appears (Run 87E) to be insufficient to prevent attack on the substrate. Pick-up of about half as much aluminum as from an unprotected alumina crucible took place.

In runs 84E and 85E the melts attacked the magnesia crucible rapidly but no magnesium contamination could be detected. This lack of contamination was due to the rapid loss of magnesium by volatilization.

2. Uranium Alloys

Information on corrosion of alumina and beryllia by uranium alloys is presented in Table 34. The contamination of the uranium by aluminum or beryllium is compared with the contamination occurring with unalloyed uranium under similar conditions.

The corrosion rate of alumina is significantly increased by the addition of 1.13 w/o zirconium, 3.75 w/o molybdenum, or 0.22 w/o thorium to uranium. For molybdenum and ruthenium the increased corrosion can be correctly ascribed to the greater wetting of the ceramic and to intergranular penetration (ANL-5602, pages 97 and 183). A significant decrease of aluminum pick-up is observed when either lanthanum or cerium alloys are melted in alumina.

Alloys containing 4.62 w/o ruthenium and 4.06 w/o molybdenum separately melted in beryllia show little change in reaction rate from the value for pure uranium interpolated from Runs 106, 107 and 108E (Table 33). With cerium alloys, however, an increase in rate by factors varying from 13 to 25 is observed. The variation seems to bear no relation to the absence of stirring in Run 111 or the differing degrees of stirring in Runs 14E and 15E.

b. The Removal of Alloying Elements from Uranium

An intensive program of experimentation has been started in which the removal of alloying elements from uranium will be studied. It is hoped that the observations will be correlatable with the ceramic oxide corrosion work already underway. Scattered results from this program are reported in Table 35. The accuracy of the results in this table is

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Table 34

CONTAMINATION OF URANIUM ALLOYS BY CRUCIBLE MATERIALS

Liquation experiments unless otherwise indicated.

Alloy: Maximum uranium impurities in preparation -
39 ppm carbon, 5 ppm nitrogen, 11 ppm oxygen

Atmosphere: Helium

Run	Crucible	Alloying Element		Melt Conditions		Contamination ^a $\mu\text{g}/(\text{cm}^2 \text{ Wetted Area})(\text{hr})$		
		Element	w/o	Nominal Temp, C	Total Time, min	Element	Alloy	Uranium ^b
65E	Al ₂ O ₃ (recrystallized)	Zr	1.13	1200	120	Al	3250	1690
91E (Top-pour)	Al ₂ O ₃ (recrystallized)	Th	0.22	1300	120	Al	6400	4850
88E	Al ₂ O ₃ (recrystallized)	Th	0.22	1300	120	Al	5325	4850
79E	Al ₂ O ₃ (recrystallized)	Mo	3.75	1200	120	Al	4950	1690
104E (Top-pour)	Al ₂ O ₃ (recrystallized)	La	0.06	1300	119	Al	3175	4850
90E (Top-pour)	Al ₂ O ₃ (recrystallized)	Ce	0.98	1200 ^c	122	Al	1525	1690
13E ^d	Al ₂ O ₃ (recrystallized)	Ce	0.98	1300	122	Al	(No Analysis)	4850
113E (Top-pour)	BeO (Slip Cast)	Ru	4.62	1300	120	Be	33	23
112E (Top-pour)	BeO (Slip Cast)	Mo	4.06	1300	125	Be	20	23
111E (Top-pour)	BeO (Slip Cast)	Ce	1.49	1300	120	Be	583	23
14E ^d	BeO (Slip Cast)	Ce	1.70	1300	122	Be	377	23
15E ^d	BeO (Slip Cast)	Ce	1.70	1300	122	Be	294	23

^aAnalytical precision (relative): Al $\pm$ 5%; Be $\pm$ 10%.

^bInterpolated values from U-Al₂O₃ kinetic studies and beryllia Runs 106, 107 and 108E, Table 33.

^cTemperature raised to 1300 C for top-pouring; hence value shown in column 9 may be underestimated.

^dInduction heated runs. No susceptor used in Run 15E.

Table 35

REMOVAL OF ELEMENTS ALLOYED WITH URANIUM
BY MELTING IN OXIDE CRUCIBLES

Alloys: Maximum impurities in preparation - 39 ppm
carbon, 5 ppm nitrogen, 11 ppm oxygen.
Atmosphere: Helium

Run	Nominal Alloy Composition ^a		Melt Conditions			Element Remaining in Ingot, Per Cent ^b
	Element	w/o	Crucible	Nominal Temp, C	Total Time, min	
128E (Top-pour)	Cerium	0.75	MgO (Slip Cast)	1200	60	70
90E (Top-pour)		0.98	Al ₂ O ₃ (recrystallized)	1200	122	90
125E (Top-pour)		1.06	Al ₂ O ₃ (recrystallized)	1300	180	30
13E ^c		1.70	Al ₂ O ₃ (recrystallized)	1300	122	25
14E ^c		1.70	BeO (Slip Cast)	1300	122	65
15E ^c		1.70	BeO (Slip Cast)	1300	122	80
99E (Top-pour)		0.98	ThO ₂ (Slip Cast)	1200	120	100
104E (Top-pour)	Lanthanum	0.06	Al ₂ O ₃ (recrystallized)	1300	119	15
65E	Zirconium	1.13	Al ₂ O ₃ (recrystallized)	1200	120	85 ^d
98E (Top-pour)		2.01	Al ₂ O ₃ (recrystallized)	1300	120	100
88E	Thorium	0.22	Al ₂ O ₃ (recrystallized)	1300	120	100
91E (Top-pour)		0.22	Al ₂ O ₃ (recrystallized)	1300	120	100
79E	Molybdenum	3.75	Al ₂ O ₃ (recrystallized)	1200	120	100

^aBalance uranium.

^bEstimated accuracy: $\pm 5\%$ for Zr, Th and Mo; $\pm 10\%$ for Ce and La. All values rounded to the nearest 5%.

^cInduction heated runs. No susceptor used in 15E.

^dQuestionable value. Some undissolved zirconium found in charge material.

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limited by analytical precision and by the homogeneity of the starting alloys. In Table 36 the composition of drosses obtained from these runs are reported.

Table 36

COMPOSITION OF DROSS FROM URANIUM
ALLOY MELTING EXPERIMENTS

Crucibles: Morgan Triangle RR recrystallized alumina.

Charges: High purity uranium.

Conditions: Helium atmosphere. Dross separated by top-pour technique.

Run	Melt Information	Element	Per Cent ^a	Per Cent Alloying Element Found in Dross
90E	Nominal Temp, 1200 C	Cerium	21.1	14
	Total Melt Time, 122 min	Uranium	71.5	
	Alloy Charge:	Oxygen	14.4	
	0.98 w/o Cerium			
91E	Nominal Temp, 1300 C	Thorium	1.06	5
	Total Melt Time, 120 min	Uranium	89.2	
	Alloy Charge:	Oxygen	10.5	
	0.22 w/o Thorium			
98E	Nominal Temp, 1300 C	Zirconium	2.33	1
	Total Melt Time, 120 min	Uranium	84.8	
	Alloy Charge:			
	2.01 w/o Zirconium			

^aEstimated relative accuracy of metal analyses $\pm 3\%$, of oxygen = 10%.
Oxygen determined on a separate sample.

The extent of removal of zirconium, thorium or molybdenum into the dross in an alumina crucible is hardly significant. There is a slight concentration of zirconium in the dross and a fivefold concentration of thorium, but these concentrations are not sufficient to effect appreciable removal. For cerium, however, the concentration into the dross is twentyfold and the fraction of the cerium found in the dross begins to be appreciable. An increase in temperature from 1200 C to 1300 C effects a much greater removal of cerium. The influence of the initial cerium content, if lanthanum is assumed to behave in a manner similar to cerium, does not seem to be large (see Runs 13E and 104E), and there would appear to be no significant trend in the results over the range 0.06 w/o to 1.70 w/o rare earth element.

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With respect to the effect of crucible material on cerium removal the rather scattered data available are consistent with the extent of crucible corrosion in the presence of cerium. This relationship will be further explored in experiments underway.

To supplement a similar study on drosses in alumina crucibles (ANL-5602, page 96) specimens of drosses from beryllia and thoria crucibles have been mounted in lucite and polished for metallographic observations. Photomicrographs of these samples are shown in Figures 23, 24 and 25. Comments on these photomicrographs are included in Table 37.

Table 37

NATURE OF DROSSES FORMED IN THORIA AND BERYLLIA

Run	Alloy Charge	Crucible	Figure Nos.	Comments
112E	U - 4.6 w/o Mo	Beryllia	Figures 23a and b	Spheroids segregated during freezing in a martensitic matrix.
110E	U - 3.95 w/o Mo	Thoria	Figure 23c	Similar to Run 112E.
113E	U - 4.62 w/o Ru	Beryllia	Figure 24a	Reaction layer absent. Acicular Ru-U intermetallic compound present in matrix.
109E	U - 4.75 w/o Ru	Thoria	Figure 24b	Similar to Run 113E.
111E	U - 1.49 w/o Ce	Beryllia	Figures 25a and b	Continuous gray crystalline platelet layer (~50 microns thick) adjacent to crucible. Unidentified dark particles in the metal layer appear to have reacted with the matrix to form a third phase.
99E	U - 0.98 w/o Ce	Thoria	Figure 25c	Reaction layer absent. Rounded gray metallic inclusions present. When etched, precipitated particles may be seen.

The major difference between these drosses and those obtained in alumina crucibles is that the molybdenum or ruthenium bearing drosses do not contain appreciable quantities of particulate matter identifiable as grains of crucible material and appear to be entirely metallic. This is also true of the cerium bearing dross in thoria. In beryllia, however, crystalline masses, presumably containing cerium oxides, are clearly evident in the dross from the cerium alloy. This dross resembles the dross from a cerium alloy melted in alumina.

FIGURE 23

MATERIAL RETAINED ON CRUCIBLE WALLS IN MOLYBDENUM ALLOY MELTS

(a) Beryllia Crucible

Uranium - 4.6 w/o Molybdenum

Magnification 100X - As Polished

(b) Beryllia Crucible

Uranium - 4.6 w/o Molybdenum

Magnification 250X - Etched

(c) Thoria Crucible

Uranium - 3.95 w/o Molybdenum

Magnification 250X - As Polished

FIGURE 24

MATERIAL RETAINED ON CRUCIBLE WALLS IN RUTHENIUM ALLOY MELTS

(a) Beryllia Crucible

Uranium - 4.62 w/o Ruthenium

Magnification 250X - Etched

(b) Thoria Crucible

Uranium - 4.75 w/o Ruthenium

Magnification 250X - Etched

FIGURE 25

MATERIAL RETAINED ON CRUCIBLE WALLS IN CERIUM ALLOY MELTS

(a) Beryllia Crucible
Uranium - 1.49 w/o Cerium

Magnification 250X - As Polished

(b) Beryllia Crucible
Uranium - 1.49 w/o Cerium

Magnification 500X - Etched

(c) Thoria Crucible
Uranium - 0.98 w/o Cerium

Magnification 250X

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2. Reactions of Uranium With Container Materials (C. Rosen, R. Sweezer)

a. Ceramic Oxides

It was found that the blackening of zirconia and thoria plaques, which results from heating them in contact with uranium, disappears on heating them to 1250 C in air, and is not affected by heating them in vacuum. This observation tends to confirm the hypothesis (ANL-5602) that the blackening is caused by a non-stoichiometric oxygen-deficient oxide (i.e., ZrO_{2-x} , ThO_{2-x}).

Preliminary observations of sessile drops of molybdenum-uranium or ruthenium-uranium alloys on thoria and zirconia plaques indicate that the contact angles are not appreciably different from those of unalloyed uranium. In contrast to this result the same alloying additions to uranium decrease the contact angles on alumina from 135° to 90°. This observation correlates with the observation that molybdenum or ruthenium additions accelerate the corrosion of alumina but not that of thoria.

b. Borides and Other Refractories

One of the prime difficulties in the utilization of materials at high temperatures is the lack of information of the nature of the processes that occur at these temperatures. To a large extent the applicability of "high temperature" materials of construction depends upon their vaporization phenomena, their thermal stability and their reactivity at these elevated temperatures.

It is not only important to know the vapor pressure of a material but also whether it vaporizes with or without decomposition. To determine this type of information an effusion apparatus has been constructed. It is fashioned after one designed by R. J. Ackermann (ANL-5482) and consists of an evacuated fused silica chamber above which is located the targets on which the evaporated species collect. The oven is heated by a 15-kw Induction Heating Corporation Vacuum Tube Generator.

The present program of investigations will include effusion measurements on TaB_2 , Ta_3B_4 , TaB , and $(Al_2O_3 + U)$. In addition, this apparatus will be used for long duration corrosion experiments with molten uranium in borided tantalum crucibles.

3. Physical Properties of Molten Uranium (C. Rosen, R. Sweezer)

One of the long-range objectives of this program is the measurement of some physical properties of uranium at high temperatures, e.g., density, surface tension, heat of fusion. At the present time photographs

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of sessile drops of uranium are being measured to determine the density of liquid uranium. The volume expansion on melting appears to be about three per cent, but this value is not reliable and will undoubtedly be refined in the next report after more precise measurements are made. The dimensions of the sessile drops will be read with a comparator microscope directly from the negative rather than from the enlargements as is presently done.

4. Phase Diagram Studies of Oxide Systems
(M. Ader, J. Bingle, D. Fredrickson)

a. Lime-Beryllia System

Efforts to obtain single crystals of the compound $2 \text{ CaO} \cdot 3 \text{ BeO}$ have not been rewarded by success. Work on the determination of atomic locations in the face-centered cubic cell ($a_0 = 14.012 \text{ \AA}$) (ANL-5602, page 107) from the powder pattern alone is proceeding satisfactorily, but it is not yet certain that unequivocal assignments will be possible.

b. Lanthana-Beryllia System
(with D. S. Flikkema)

Thermal analysis experiments within the range 15 to 45 mole per cent lanthana have confirmed the observation (ANL-5602, page 109) that there exists at least one eutectic melting within the range 1360 to 1372 C. However, efforts to determine the liquidus in this region were unsuccessful and indicated that revision of the apparatus to provide stirring and seeding of melts, larger charges and higher temperatures will be required for this part of the study.

Two distinctly different X-ray powder patterns have been obtained from mixtures held in platinum crucibles for several hours at 1450 to 1500 C in air. Lanthana or beryllia lines were not seen in either pattern. The first pattern was found for starting compositions containing 15, 20 and 25 mole per cent lanthana; the second, for starting compositions containing 30, 35, 40 and 45 mole per cent lanthana. Neither pattern has been definitely indexed as to lattice type. However, in one experiment with a 35 mole per cent lanthana mixture some large crystals were found on cooling from the melt. The crystals were examined microscopically and were found to be elongated prismatic monocrystals, classified as hexagonal or pseudo-hexagonal. The refractive indices are greater than two, and the birefringence (uniaxial negative) is weak, n_w being greater than n_e by 0.016. Other fragments from the solidified melt were opaque and thus gave no additional information on microscopic examination. However, the X-ray powder patterns of both the opaque fragments and the single crystals were identical. Further work is planned to determine the homogeneity range, crystal class and lattice constants of this phase.

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5. Magnesium Extraction Studies

With a view toward potential separations process applications, work is being continued on the extraction of plutonium from uranium by liquid magnesium.

a. Extraction from Powdered Uranium (R. Nuttall, J. Settle)

Work reported earlier (ANL-5602, page 110) had demonstrated the extraction of plutonium in tracer concentrations from powdered uranium prepared by the hydriding-dehydriding cycle. The extraction of plutonium from uranium-1 w/o plutonium alloy has been tested by contacting powdered alloys with liquid magnesium. The apparatus was similar to that already described.

Analytical results from one run are available and are given in Table 38.

Table 38

EXTRACTION OF PLUTONIUM FROM POWDERED URANIUM-PLUTONIUM ALLOY

Run No.: 24
Temp: 800 C
Contact Time: 1 hr
Charge: 10.470 g Mg; 51.102 g U-1 w/o Pu

	<u>Per Cent Extracted into Mg</u>	<u>Material Balance</u>
U	0.001	98.2
Pu	48.0	94.0

By comparison with earlier tracer results it may be seen that the ability of magnesium to extract significant quantities of plutonium has not been lost despite a sharp increase in the amount of plutonium present and a large decrease in the ratio of magnesium to uranium. Further experiments to determine the factors responsible for the extent of extraction are underway. Apparatus for repeated contacts of liquid magnesium with powdered uranium is being constructed.

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b. Extraction of Plutonium from Molten Uranium
(E. Greenberg, M. W. Nathans, K. E. Anderson)

Equilibrium partition data obtained in static experiments for the uranium-plutonium-magnesium system have now been supplemented by data obtained in an induction-heated set-up wherein a greater degree of mixing prevails. Analytical data for four induction-heated runs have been gathered. In addition, seven runs have been made with uranium - 5.2 w/o chromium - 1 w/o (nominal) plutonium alloy as the heavy metal phase. Samples from two of the latter groups of runs were spoiled and no results could be obtained from them. Table 39 gives the conditions under which the runs were made. Table 40 summarizes the available analytical results. Table 41 summarizes the partition ratios for plutonium obtained from the experiments made with uranium-1 w/o plutonium alloys.

Table 39

EXPERIMENTAL CONDITIONS FOR MAGNESIUM EXTRACTION RUNS

Initial Alloy Compositions: U-Pu, 0.92 w/o Pu; U-Pu-Cr,
5.35 w/o Cr, 0.83 w/o Pu,
91.2 w/o U.

Run No.	Heavy Phase	Temp (C)	Time at Temp (hr)	Wt Mg Charged (g)	Wt Mg in Capsule After Run, g	Wt U (g)	Wt Pu (mg)
31	U-Pu	1190	1½	18.01	1.0	12.30	113
32	U-Pu	1190	3	18.18	1.6	12.22	112
33	U-Pu	1195	6	18.09	3.8 ^a	12.74	117
34	U-Pu	1180	3	18.18	1.6	10.44	95
37	U-Pu-Cr	905	3	18.21	0.6	9.59	80
38	U-Pu-Cr	1195	3	18.14	1.7	13.78	115
39	U-Pu-Cr	1055	3	18.03	0.5	19.30	160
40	U-Pu-Cr	1010	3	20.59	0.2	10.69	89
41	U-Pu-Cr	960	3	19.79	0.1	14.39	119
42	U-Pu-Cr	1100	3	20.31	0.4	11.59	96
43	U-Pu-Cr	1150	3	20.42	-	8.04	67

^aObtained by extrapolation from the values for Runs 31, 32, 34.

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Table 40

ANALYTICAL RESULTS FOR MAGNESIUM EXTRACTION
OF PLUTONIUM FROM MOLTEN URANIUM

For conditions see Table 39.

Run No.	Plutonium Found					Uranium Found			Chromium Found	Magnesium Determined
	in Mg, mg	in U, mg	in Residue, mg	Total mg	% of Charge	in Mg, g	in U, g	in Residue, g	in Mg, mg	in Mg Phase, g
31	77.0	34.8	-	112	99	0.16	11.8	-	-	14.0
32	75.8	32.9	-	109	97	0.45	11.4	-	-	12.3
33	74.0	32.6	-	107	92	0.32	11.7	-	-	10.3 ^a
34	65.8	24.1	1.7	92	96	0.30	9.8	0.049	-	12.0
37	53.3	7.5	10.1	71	89	0.14	8.4	0.22	47	16.8
38	68.5	36.5	9.1	114	99	0.27	12.1	0.27	53	10.7
39	90.4	24.4	35.3	150	94	0.12	16.9	0.33	35	13.8
41	56.0	23.4	32.4	111	93	0.050	12.6	0.35	27	17.0
42	56.8	22.8	15.6	95	99	0.10	9.1	0.74	66	16.8

^a3.8 g of Mg was recovered from the cover and crucible chips.

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Table 41

DISTRIBUTION OF PLUTONIUM BETWEEN
URANIUM AND MAGNESIUM AT 1190 C

For conditions and primary data see Tables 39 and 40.

Run No.	Temp (C)	Time at Temp (hr)	Wt of U ^a (g)	Wt of Mg ^b (g)	$\frac{\text{mg Pu}}{\text{g U}}$	$\frac{\text{mg Pu}}{\text{g Mg}}$	Apparent Partition Ratio ^c
31	1190	1 $\frac{1}{2}$	12.0	17.0	2.90	4.53	0.15 ₉
32	1190	3	11.7	16.6	2.82	4.57	0.16 ₅
34	1180	3	10.1	16.6	2.39	3.96	0.17 ₁
33	1195	6	12.3	14.2	2.65	5.21	0.20 ₁

^aCharged weight less amount found in the Mg phase.

^bCharged weight less amount found in the capsule.

^cPartition ratio = mole fraction of Pu in Mg phase $\div$ mole fraction in U phase.

The plutonium concentration in the magnesium phase is based on the charged weight of the magnesium less the weight of magnesium lost to the capsule as a result of vaporization. The plutonium concentration in uranium phase is based on the charged weight of uranium corrected for the amount of uranium found in the magnesium phase after the extraction. Besides the non-systematic errors of analysis, which are approximately 2 per cent for plutonium and 0.5 per cent for uranium, the calculated values of partition ratios may have the following sources of error:

- (a) After dissolution of the magnesium phase in dilute sulfuric acid a small amount of residue is usually left. This residue is dissolved in aqua regia and the solutions are combined. In Run 34 the residue was submitted separately for analysis. Less than three per cent of the plutonium present in the magnesium phase was found, in agreement with earlier work. However, this degree of uncertainty in the final results persists because it is not evident whether or not the residue represents material dissolved in magnesium during equilibration.
- (b) No correction was made to the data for the amount of magnesium which condenses and forms stationary droplets on the walls and cover of the crucible as a

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result of temperature gradients existing in the furnace during the run. It is estimated that less than 0.5 g of magnesium is condensed there and therefore does not participate in the equilibration. A larger amount of magnesium is found on the crucible walls and cover after the conclusion of the experiment but it can be shown that the bulk of this is the result of distillation during cooling.

- (c) The material balance for uranium is approximately 97 per cent. It is uncertain whether this is caused by a bias in the analysis itself or by a uranium loss.
- (d) The amount of uranium found in the magnesium phase, which ranges from one to three per cent, is higher than the literature value for the solubility of uranium in magnesium, 0.14 per cent. It is suspected that this is caused by the presence of very small droplets of uranium trapped in the magnesium. A small mechanical carry-over of plutonium results.

The possible errors discussed under (b) and (c) are of the same order of magnitude but in opposite directions and tend to cancel. The possible errors discussed under (a) and (d) each tend to increase the apparent partition ratio by a maximum of about two per cent.

The agreement between the results of Runs 32 and 34 appears to be within the described limits of error. The trend of the partition ratios with time of contact appears to be real and significant of a true equilibrium value somewhat in excess of 0.20. Additional runs of longer duration are in progress.

The analytical results tabulated in Table 40 for the experiments made with the chromium alloy show the presence of 10 to 30 per cent of the plutonium in the residues from the dissolution of magnesium. It is obvious that under these circumstances no confidence can be placed in any partition ratio one might attempt to calculate from the data. Experiments are currently underway to eliminate the conditions which cause the formation of this residue.

c. Extraction of Fission Products from Uranium Alloys
(G. Elliott)

Equipment and techniques have now developed for the study of the distribution of added constituents between immiscible liquid metallic phases at temperatures up to 950 C. Such a study of the distribution of ruthenium between magnesium and uranium - 11 w/o iron has been nearly completed.

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1. Experimental

a. Equipment

Three major components of the equipment provide controlled resistance heating to 950 C, mixing of the liquid phases by shaking, and a method for performing the required equilibrations in an inert atmosphere.

- (a) The furnace is heated by ten 300-watt nichrome resistance heating elements. Eight elements operate from a 200 v - 20 amp variable auto-transformer to give gross control of the power input; two elements, operating intermittently through a thermocouple temperature controller, give fine temperature control. The temperature of a chromel-alumel thermocouple mounted near the samples is recorded automatically. The hot zone of the furnace is 8 x 13 x 12 inches deep and is surrounded by K-28 firebricks.
- (b) An Inconel sample carrier arm operates through a small hole in the side of the furnace. The sample carrier rotates at 40 rpm on an oval path. The width of the oval is constant but the length, and correspondingly the vigor of shaking, is controlled by the position of a sliding pivot outside the furnace and a fixed mechanical drive. The maximum acceleration attainable is up to 100 cm/sec in 0.4 sec.
- (c) The samples were loaded into capsules in the following manner. Weighed metal charges (usually 20 grams of each alloy) were put into crucibles with fitted, ground covers and these in turn were placed in a Vycor tube fitted with a rubber stopper at the upper end and necked-down section at the lower end. The crucibles were supported with packed quartz wool. Above the uppermost crucible was placed a short, closed-end section of Vycor tubing having an outer diameter only slightly smaller than the inner diameter of the outer tube. The capsule was then evacuated and the outer tube shrunk on the inner with an oxy-hydrogen flame to form a seal. The contents of the capsule were then out-gassed by flaming at a pressure of one micron. At the conclusion of this operation 25 cm of argon was admitted to the capsule and the final sealing was accomplished by collapsing the narrow lower stem.

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b. Performance

In this apparatus tantalum crucibles attain a steady temperature in about 45 minutes and ceramic crucibles in about 90 minutes. The outgassing procedure appeared to be adequate to insure microscopically smooth, dross-free interfaces between the solidified light and heavy metals. The penetration of magnesium through the walls of magnesia crucibles depends on the porosity of the ceramic. With finely grained, slip-cast magnesia ware the attack by the escaping magnesium vapor on the Vycor capsule appeared to be negligible.

c. Preparation of Samples for Analysis

Samples of the equilibrated phases were obtained by cutting the bulk metals away from each other and from the crucible with a rubber-bonded carborundum wheel. Foreign inclusions, formed by the trapping of droplets between the crucible wall and the bulk metal, were ground off. The analyses for ruthenium involved its colorimetric estimation as ruthenate after distillation as the tetroxide.

2. The Distribution of Ruthenium

The solubility of ruthenium¹⁹ in magnesium has been reported to be equal to or greater than 20 w/o at 800 C. As a preliminary to this study it was desired to ascertain the readiness with which ruthenium dissolves in magnesium. Two samples, each containing 10.5 w/o ruthenium, were prepared. In one the ruthenium was in the form of the as-received fine powder and in the other the ruthenium was in the form of a pellet. The pellet was formed by compression of the powder at 20,000 psi, firing in hydrogen, followed by sintering at 1650 C in vacuum. The samples were heated, with shaking, for four hours at 800 C. Microscopic examination of polished sections of the ingots revealed no perceptible difference between the two. The appearance of the coarse, crystalline aggregates which are uniformly dispersed in the magnesium matrix indicates the precipitation of an intermetallic compound from solution on cooling. An effort is being made to determine the composition and X-ray diffraction pattern of the presumed intermetallic compound by isolating it through differential solution of the matrix.

Twenty experimental equilibrations were performed, with results shown in Table 42. Series A shows that transfer of ruthenium from light to heavy phase occurs quite rapidly. In experiment 10-1-E more than 99% of the ruthenium transferred in one hour at temperature; in experiment 18-2-E 41% of the available ruthenium had diffused from liquid magnesium into uranium-iron in one-quarter hour despite the fact that the latter had

¹⁹Gilman, A. R. and Isserow, S., NMI-1139 (April 1955).

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Table 42

THE DISTRIBUTION OF RUTHENIUM BETWEEN MAGNESIUM
AND URANIUM - 11 w/o IRON

Run No.	Temp (C)	Time at Temp (hr)	Crucible	Final Concentration Ru in Heavy Phase (Mole Fraction x 10 ³)	Partition Ratio ^a (x 10 ⁴)
<u>Series A:</u> Ruthenium initially dissolved in magnesium					
10-1-E	805	1	Ta	3.8	6 ^d
11-1-E	803	8	Ta	1.9	-
18-2-E	730	1/4	MgO	118	- ^b
19-2-E	798	1/2	MgO	89	-
<u>Series B:</u> Ruthenium initially dissolved in uranium-iron					
10-2-E	805	1	Ta	3.9	9 ^d
11-2-E	803	8	Ta	4.0	-
18-1-E	730	1/4	MgO	110	- ^b
19-1-E	798	1/2	MgO	77	8.2, 8.7
<u>Series C:</u> Ruthenium added to mixture					
12-1-E	799	6	Ta	1.3	-
12-2-E	799	6	Ta	5.4	-
13-1-E	799	6	Ta	29	5.4, 5.7
13-2-E	799	6	Ta	87	2.6, 1.2, 1.6 ^c
14-1-E	805	1 1/2	MgO	125	85, 85 ^c
14-2-E	805	1 1/2	MgO	84	12, 13
15-1-E	921	1 1/2 ^c	MgO	125	19, 19
15-2-E	921	1 1/2 ^c	MgO	81	14, 14
16-1-E	857	1	MgO	124	6.2, 6.2 ^c
16-2-E	857	1	MgO	84	-
17-1-E	750	4	MgO	125	13
17-2-E	750	4	MgO	80	6.3, 6.4

^aMole fraction Ru in Mg ÷ mole fraction Ru in U-Fe.

^bHeavy phase only partially melted.

^cQuestionable values.

^dOnly the upper limit was determinable because of limitation of analytical technique.

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only partially melted. Experiment 19-1-E of Series B demonstrates that extraction in the reverse direction took place in one-half hour at temperature to an extent consistent with the more comprehensive Series C tests. It appears reasonable, therefore, to consider that the data represent equilibrium partitions. However, it should be stressed that the analysis for milligram quantities of ruthenium in gram quantities of magnesium has been subject to some difficulties which may be the cause of systematic error in the partition ratios quoted. With this limitation in mind the trend of the most reliable results appears to show effects of both concentration and temperature as exemplified in Tables 43 and 44, respectively. No specific effect of crucible material is apparent.

Table 43

PARTITION RATIO OF RUTHENIUM BETWEEN MAGNESIUM AND
URANIUM-IRON AS A FUNCTION OF CONCENTRATION

<u>Exp No.</u>	<u>Temp (C)</u>	<u>Final Conc. in Heavy Phase (Mole Fr x 10³)</u>	<u>Partition Ratio (x 10⁴)</u>
10-1-E	805	3.8	6
10-2-E	805	3.9	9
13-1-E	799	29	5.4, 5.7
19-1-E	798	77	8.2, 8.7
14-2-E	805	84	12, 13

Table 44

PARTITION RATIO OF RUTHENIUM BETWEEN MAGNESIUM AND
URANIUM-IRON AS A FUNCTION OF TEMPERATURE

<u>Exp No.</u>	<u>Temp (C)</u>	<u>Final Conc. in Heavy Phase (Mole Fr x 10³)</u>	<u>Partition Ratio (x 10⁴)</u>
17-2-E	750	80	6.3, 6.4
19-1-E	798	77	8.2, 8.7
15-2-E	921	81	14, 14

The only other values available to us for the distribution of ruthenium are the data of Motta.²⁰ At 1150 C the partition ratio of tracer ruthenium between magnesium and molten uranium varied between 11×10^{-4} and 110×10^{-4} as the concentration of ruthenium varied from parts per billion to parts per million. The difference of temperature, concentration and heavy metal phase nature between Motta's results and ours allows no further comparison.

²⁰Motta, E. E., P/542, Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Vol. 9, Geneva, 1955.

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

1. Design and Testing of Components for Pilot Plant
(G. J. Bernstein, L. Weaver, V. N. Thelen)

Evaluation was continued for various alternative equipment designs considered for use in the EBR-II pyrometallurgical pilot plant.

a. Development of Top-Pour Crucible

Two models of top-pour crucible assemblies were tested, principally for coil current requirements and coil operating temperatures. The use of a graphite (7-3/4 inch OD) susceptor cemented into a transite pipe (11-3/4 inch OD) with Alfrax cement required excessively high operating currents in a coil around the outside of the transite because of poor coupling. Satisfactory coupling was realized with a refractory sleeve coil support which permitted use of a coil with a 9-1/4 inch ID. The coil support is an externally grooved cylinder (7 inches ID x 9 inches high x 1 inch thick) fabricated at Los Alamos from a mix made of Babcock and Wilcox K-30 firebrick. It has exhibited good mechanical strength and resistance to thermal shock. With uncooled 5-turn and 6-turn 3/8-inch induction coils, maximum coil temperatures were around 550 to 600 C at power levels of 5.4 kw and coil currents of 225 amperes. This was sufficient power to maintain a crucible at 1200 C.

b. Performance of Uncooled Induction Coils and Leads

It is desirable in the top-pour furnace to tilt the entire crucible assembly including the coil. This means that flexible coil leads or a method for remotely disconnecting the coil within the furnace chamber must be used. Both of these procedures were tested in the last quarter. Flexible leads, 32 inches long and made of 48 strands of 22-gage nickel-plated copper wire twisted together, attained temperatures of 221 C and 384 C at power levels of 6.9 and 12 kw (202 and 267 amp). These are not considered excessive and the use of flexible, uncooled, induction power leads appears practical.

As a means of remotely disconnecting the coil within the furnace chamber, insertion and removal of coil leads from vessels containing a molten metal is a feasible procedure. It has the disadvantage that power must be interrupted for pouring. Wood's metal has been used to make connections between solid bus bars and the coil. These connectors remained fairly cool, reaching temperatures of only 70 C at power levels of 12 kw.

c. Cast Protrusion Sampling of Uranium Ingots

A proposed method for sampling ingots cast after pyrochemical processing is to use a mold which casts a small protrusion on the base of the ingot. This protrusion can be broken off and chemically analyzed for metal composition. Three tests were made to check the feasibility of casting such protrusions and to compare analyses of the protrusions with samples taken of the melt itself.

The melt consisted of approximately 6 kg of uranium with a small amount of iron added as a solute. The ingots were cast into a graphite mold which had in its base 5 holes $5/32$ inches in diameter and $3/8$ inches deep. In two of the runs all five protrusions cast full and clean. In one run, one protrusion failed to cast. As may be seen in Table 45, the analyses of the protrusion samples were in close agreement with each other and with the direct melt sample.

Table 45

COMPARISON OF ANALYSES OF PROTRUSION CAST
SAMPLES AND MELT SAMPLES

Run No.	Melt Sample % Fe	Protrusion Sample (% Fe)					Average
		No. 1	No. 2	No. 3	No. 4	No. 5	
34	0.0115	0.0113	a	a	a	a	-
35	0.0188	0.0186	a	a	a	a	-
37	1.20	1.19	1.17	1.19	1.18	1.21	1.19
	1.20	1.20	1.18	1.20	1.18	1.22	

^aAnalyses not made on these samples because of difficulty of analysis at low iron concentration.

2. Melting of Sodium-Coated Uranium Pins
(G. Bernstein, G. Bennett, W. Kline, V. N. Thelen)

In the EBR-II reactor, a thin (6-mil) heat transfer ligament of sodium is used between the uranium fuel pin and the stainless steel jacket. On removal of the jacket, a portion of the sodium adheres to the pin and may be present during the subsequent melting operation. It is of interest to determine the effect of sodium in this operation.

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Accordingly, 1/8-inch diameter by 2-inch long uranium pins were coated with sodium by soaking them in sodium at 300 C for about four hours* under a relatively impure inert atmosphere. The uranium pins were blackened by reaction with sodium oxide dissolved in the sodium and being continuously formed at the surface. The formation of uranium oxide on the surfaces of the pins was felt to be more extensive than that which would occur in the processing cell.

In initial experiments involving about 750 grams of rods, incomplete melting and coalescence of the melted material occurred. It was apparent that in some cases the melted uranium was retained by the oxide skin. However, in a half dozen subsequent experiments using 2-kg charges, melting and consolidation of the molten metal was effected. In the last of these a clean ingot constituting 93.3 per cent of the charge was poured. A yield of 95.5 per cent resulted from a melt of pins which initially had a light oxide coating but were not contacted with sodium. Because of superior atmosphere purity conditions which can be achieved in the processing facility, it is not expected that the presence of the sodium film will prevent melting of the fuel pins.

In the course of this work, coalescence of pins was easily achieved by reduction of any oxide film with calcium in the presence of a flux of calcium chloride or barium chloride. The addition of magnesium at a temperature of around 1100 C also was promising. From the standpoint of subsequent fission product removal, the use of magnesium is the more attractive since it is rapidly vaporized. However, recourse to either procedure is undesirable and now appears unnecessary.

3. Control of Dross in Melt Refining (G. Bennett, W. Kline)

This is a cooperative program with the laboratory group (see page 92 of this report) in which the main efforts of the semi-works have been:

- (1) preparation of various uranium alloys of interest, and
- (2) investigation of the effect of inductive mixing on crucible erosion by repeating in an induction furnace certain drossing runs previously performed in the laboratory resistance-heated Stokes furnace.

*As a sidelight, it was noted that with the addition of as little as 0.5 wt per cent calcium (the minimum amount tried) to the sodium, wetting of the uranium pins was effected in 5 minutes as contrasted to 3 to 4 hours with pure sodium.

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a. Preparation of Uranium Alloys

Table 46 gives a comparison of the nominal and analyzed compositions of special alloys which have been prepared for drossing experiments reported on page 96. This program is now complete.

Table 46

ANALYSES OF URANIUM ALLOYS FOR LABORATORY
DROSSING EXPERIMENTS

<u>Run No.</u>	<u>Sample Location</u>	<u>Nominal Composition (Weight Per Cent)</u>	<u>Analyzed Composition (Weight Per Cent)</u>
AL-9a	Top Edge	4.1 Mo	3.73 Mo; 0.0051 Al ^a
	Bottom Edge		3.76 Mo; 0.0014 Al
AL-10a	Top Edge	2.3 Cr	1.67 Cr
	Bottom Edge		1.76 Cr
AL-11a	Top Edge	1.5 Th	0.19 Th; 0.0030 Al ^a
	Bottom Edge		0.22 Th; 0.0025 Al ^a
AL-12a	Top Vertical Slice	2.2 Ce	0.76 Ce; nil Al ^a
	Bottom Vertical Slice		0.98 Ce; nil Al ^a
AL-13a	Top Vertical Slice	2.0 Zr	2.01 Zr
	Bottom Vertical Slice		2.08 Zr
AL-14b	Top Vertical Slice	1.1 La	0.059 La; 0.0020 Al ^a
	Bottom Vertical Slice		0.036 La; 0.0019 Al ^a
AL-17a	Top Vertical Slice	4.1 Mo	3.95 Mo
	Bottom Vertical Slice		4.06 Mo
AL-18a	Top Vertical Slice	3.6 Ru	3.45 Ru
	Bottom Vertical Slice		4.98 (being checked)
AL-19a	Top Vertical Slice	2.9 Ce	1.70 Ce; 0.0021 Al ^a
	Bottom Vertical Slice		1.49 Ce; 0.0016 Al ^a

^a Alumina present in original uranium

The data reported in Table 46 show generally good agreement between analyses of different sections of the same ingot. The nominal and analyzed compositions are often different. The greatest variations occur in the case of the thorium and lanthanum alloys, which contain smaller percentages of alloying element than desired. These results can possibly

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be explained by slagging out of the thorium, and segregation of the lanthanum. Success in making cerium alloys of the indicated concentration is gratifying. In all cases the amount of aluminum present was determined in order to provide a base point from which to calculate crucible corrosion rates in laboratory experiments.

b. Induction Heating Dross Experiments

Additional results are now available on the effect of induction heating on crucible erosion. A comparison of certain induction heated runs using high purity uranium with similar drossing runs made by the laboratory group in the resistance heated Stokes furnace is given in Table 47.

Table 47

EFFECT OF INDUCTIVE MIXING ON CRUCIBLE EROSION
(High purity Morganite alumina crucibles)

Type of Heating	Temp (C)	Time of Temp (hr)	F ^a	Crucible Erosion (gm Al/cm ² wetted surface)
Resistance ^b	1200	2	-	0.0051 ^c
Induction	1200	2	0.28	0.0043, 0.0079
Induction	1200	2	0.53	0.0051
Resistance ^b	1300	2	-	0.015
Induction	1300	2	0.28	0.0125
Induction	1300	2	1.00	0.018

^aF = calculated fraction of current penetrating charge.

^bFrom Figure 27, ANL-5602

^cThis figure incorrectly reported in ANL-5602 as 0.036.

As indicated in the above table, little effect of inductive mixing on crucible erosion is apparent with high purity uranium. Some additional experiments are planned to ascertain the effect of the solute elements, ruthenium and molybdenum, since these change the character of the oxide dross (see page 100).

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4. Reactions of Fissium in the EBR-II Cell Atmosphere
(A. A. Chilenskas, D. D. Busch*)

It is expected that fuel pins and ingots of fissium, which may attain temperatures up to 600 C, will have to be stored in the cell atmosphere for considerable periods of time. The question of how much reaction might be expected when fissium is thus exposed to a cell atmosphere containing a nominal 1000 ppm oxygen and 5 per cent nitrogen at a temperature of 600 C has been investigated. Under this condition, the reaction rate was 17.8 mg U_3O_8 produced per sq cm per hour. Reduction of the oxygen concentration to 155 ppm reduced the reaction rate to 4.5 mg U_3O_8 /(sq cm)(hr)(see Table 47). Virtually no nitride was formed. Extrapolation of these data to 10 kg each of fuel pins (6600 sq cm of area) and a cast ingot (377 sq cm of area) indicates the following reaction rates:

<u>Per Cent Uranium Reacting Per Hour</u>		
<u>Oxygen Conc (ppm)</u>	<u>Fuel Pins</u>	<u>Cast Ingot</u>
945	0.86	0.045
155	0.22	0.013

These calculated reaction rates are probably higher than would occur in the cell because oxygen will not be so readily available in the cell as in the experiment because of its depletion in the near vicinity of the stored material. However, it is apparent that the oxidation of uranium must be limited to values considerably lower than those calculated above, especially for the fuel pins. Consequently, it has been decided that the pins will be dispersed to keep their temperature as low as possible and stored in an atmosphere of very low oxygen concentration, such as in the gas being returned to the cell from the oxygen purification unit.

The fissium ingots used in this study were obtained by sectioning a single ingot cast into graphite and cooled under a helium atmosphere. The analysis of this ingot was:

	<u>Weight Per Cent</u>			
	<u>Ru</u>	<u>Pd</u>	<u>Mo</u>	<u>Zr</u>
Top Slice	2.48	0.211	3.32	0.080
Bottom Slice	2.56	0.186	3.22	0.267

The apparatus used is shown schematically in Figure 26. Experimental results are given in Table 48.

*Student Aide, summer employee.

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FIGURE 26

APPARATUS USED IN DETERMINING OXIDATION RATE OF FUEL PINS
Experimental Results are given in Table 48

Table 48

REACTIONS OF FISSIUM IN IMPURE ARGON ATMOSPHERE

Temperature: 600 C
Time at 600 C: 69 hr
Argon Rate: 740 ml/min

Oxygen (ppm)	Nitrogen (Vol %)	Ingot Wt (gm)	Ingot Wt Gain (gm)	N ₂ Content of Reacted Mat'l (ppm)	Reaction Rate (mg U ₃ O ₈ /(cm ²)(hr))
945	5	27.591	2.043	118	17.8
155	5	32.951	0.530	677	4.5

A quantitative indication of the reaction rate during the entire course of the run was obtained by monitoring continuously the oxygen in the effluent stream. The indication was that except for the first several hours, when the reaction rate was somewhat higher, the reaction rate was essentially constant over the entire run.

5. Control of Volatile Fission Products (J. Wolkoff, J. Jones, W. Jones)

The testing of materials having potential value for the retention of volatile fission products (excluding the noble gases) has continued in the equipment described in the last quarterly report (ANL-5602, p. 120).

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Attention has been directed exclusively to retention of alkali metals, with sodium being used as a typical alkali metal. Nine materials have been found that are effective in retaining sodium vapor. All of these are either high surface area materials or materials chemically reactive with alkali metals.

Table 49 is a summary of the runs made in the last quarter. The runs have been grouped according to bed materials to show similarities or contrasts. Bed materials are described in the footnotes.

Two types of runs have been used for evaluating bed materials. The first type consisted of:

- (1) Degassing of bed material under vacuum to the temperatures shown until pressure fell to 0.1 mm or less.
- (2) Vaporization of sodium for 30 minutes at a pressure of 0.4 mm and a crucible temperature of 400 C. The temperature and pressure were adjusted in some runs to give equivalent vaporization conditions.
- (3) A "retention" test was performed in some of the runs where no sodium leakage occurred by raising crucible temperature slowly to 800 to 900 C and observing if and when sodium deposits formed.

The second type differed mainly in that sodium vaporization and retention was effected at atmospheric pressure, conditions being as follows:

- (1) Same degassing procedure.
- (2) Vaporization at atmospheric pressure under argon as the crucible temperature was slowly raised and held briefly at 550, 650, 750, 880 and 900 C.
- (3) In Runs 26 and 27 a modified "retention" test was performed by evacuating the system to 100 mm of mercury at 900 C after completion of the previous part.

Bed materials are categorized as "effective" or "ineffective" in retaining vaporized sodium as follows:

Effective ($> 99.9\%$ retention of sodium)		Ineffective ($< 99.9\%$ retention of sodium)
"Molecular sieves"	Activated carbon	Refractory magnesia
Activated alumina	Coconut charcoal	Refractory zirconia
Activated bauxite	Silver chloride	Refractory alumina
Activated magnesia	CuCl on charcoal	"Fiberfrax" wool
Fuller's earth	AgCl on charcoal	Diatomaceous silica
		Silica gel

Table 49

TESTS OF GRANULAR BEDS FOR RETAINING VAPORIZED ALKALI METAL

Bed: 1-5/8 inch diameter x 2 inches deep
(Sodium used in all runs except 18, in which cesium was used.)
(Equipment description on page 120, ANL-5602)

Run No.	Bed Material	Max Degas Temp, C	Vaporization Conditions			Deposit ^a	Retention Conditions		
			Crucible Temp, C	Top of Bed Temp, C	Average Pressure, mm		Max Crucible Temp	Max Top Temp	Deposit ^a
A. Refractory Materials									
12	14/24 mesh magnesia ^a	630	400	200 - 300	0.4	Yes	-	-	-
13	8/24 mesh zirconia ^b	650	400 - 430	155 - 240	0.4	Yes	-	-	-
28	4/10 mesh alumina ^c	525	500 - 700	265 - 430	760	Yes	-	-	-
B. Sorbent Materials									
15	3/8 mesh silica gel	515	395 - 450	205 - 310	0.4	Yes	-	-	-
17	3/8 mesh silica gel	410	400 - 420	290 - 310	0.4	Yes	-	-	-
21	0.175-in diameter diatomaceous silica ^d	550	370 - 480	320 - 375	0.4	Yes	-	-	-
22	0.175-in diameter diatomaceous silica ^d	550	400 - 490	215 - 235	0.4	Yes	-	-	-
23	1/8-in activated alumina ^e	420	400 - 460	400 - 420	0.4	Yes	-	-	-
35	1/8-in activated alumina ^e	395	420	210 - 260	0.4	No	805	460	No
27	1/4-in - 8 mesh activated alumina ^f	510	550 - 900	-	760	Trace	-	-	Trace
30	4/8 mesh activated bauxite ^g	645	560 - 900	330 - 530	760	Trace	-	-	-
16	4/8 mesh Fuller's Earth ^h	540	380 - 405	240 - 260	0.4	Trace	800	460	Trace
11	1/8-in Molecular Sieves ⁱ	515	400	230 - 250	0.4	No	915	485	Trace
18 ^r	1/8-in Molecular Sieves ⁱ	530	245 - 260	140 - 160	0.4	No	810	470	No
14	6/14 mesh activated carbon ^j	555	415 - 425	250 - 270	0.4	No	600	360	No
26	6/8 mesh activated carbon ^k	605	550 - 900	270 - 450	760	Trace	-	-	Trace
29	6/14 mesh coconut charcoal ^l	510	400 - 420	210 - 300	0.4	No	800	560	No
33	6/14 mesh coconut charcoal ^l	615	550 - 900	340 - 545	760	Trace	-	-	-
20	silver chloride ^m	395	360 - 375	185 - 190	0.2	No	-	-	-
36	AgCl on coconut charcoal ^p	570	550 - 900	310 - 505	760	Trace	-	-	-
37 ^s	AgCl on charcoal plus activated carbon ^q	750/500	550 - 900	230 - 465	760	Trace	-	-	-
29	CuCl on activated carbon ⁿ	None	550 - 900	330 - 545	760	Trace	-	-	-
34	CuCl on coconut charcoal ^o	410	550 - 900	330 - 510	760	Trace	-	-	-

*Any sodium not retained by the bed material or later given up by the bed material was detectable by the formation of a sodium deposit (a film or mirror) on the Vycor bell jar enclosing the apparatus.

Description of Bed Materials

- 14/24 mesh magnesia, "Magnorite" fused magnesia grain, Norton Co.
- 8/24 mesh zirconia, Type I fused lightweight zirconia, Norton Co.
- 4/10 mesh alumina, fused bubble alumina, screened 1/16- to 1/8-inch diameter spheroids from Alfrax 58, Carborundum Co.
- 0.175-inch diameter diatomaceous silica, "Celite" 408 extruded pellets 0.175-inch diameter x 0.156-inch long, Johns-Manville.
- 1/8-inch activated alumina, H-151 grade alumina beads, 1/8-inch diameter spheroids, Alcoa.
- 1/4-inch - 8 mesh activated alumina, F-10 grade alumina, Alcoa.
- 4/8 mesh activated bauxite, "Florite" brand, Floridin Co.
- 4/8 mesh Fuller's earth, "Florex" brand, Floridin Co.
- 1/8-inch Molecular Sieves, 4A grade extruded pellets, 1/8-inch diameter x 3/8-inch long, Linde Air Products Co.
- 6/14 mesh activated carbon, "Columbia" Type AC granular, National Carbon Co.
- 6/8 mesh activated carbon, "Columbia" Type SXC extruded pellets 0.118-inch diameter, National Carbon Co.
- 6/14 mesh coconut charcoal, granular.
- Silver chloride, 1/4-inch granular agglomerates of reagent grade powder.
- CuCl on 4/6 mesh activated carbon, Type CXA activated carbon (0.171-inch diameter extruded pellets, National Carbon Co.) impregnated with CuCl₂, dried and heated in argon to 1000 C, estimated loading 0.14 g CuCl/g carbon.
- CuCl on coconut charcoal, 6/14 mesh coconut charcoal impregnated with CuCl₂, dried and heated in argon to 900 C, estimated loading 0.35 g CuCl/g charcoal.
- AgCl on coconut charcoal, 6/14 mesh coconut charcoal impregnated with AgCl from HCl-AgNO₃ reaction, 0.61 g AgCl/g charcoal.
- AgCl on charcoal plus activated carbon; total bed height, 4 inches, lower half AgCl impregnated on 6/14 mesh coconut charcoal, 0.37 g AgCl/g charcoal; upper half Type SXC 6/8 mesh activated carbon.
- Cs used this run.
- Bed 4 inches deep this run.

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High surface area materials have retained all or practically all the vaporized sodium in the bed while refractory materials have not. The refractory bed materials hold back some sodium by condensation due to the temperature gradient across them, but this effect is augmented greatly with bed materials of high surface area and porosity. The nature of the increased effectiveness has not been systematically investigated but present indications point to physical adsorption plus at least part chemical absorption. The silica gel and diatomaceous earth are interesting exceptions to the enhanced retention associated with high surface area and porosity.

The copper chloride and silver chloride listed are alternative methods and depend for effectiveness on chemical reaction between alkali metal vapor and the salt. A bed composed of granules of pure silver chloride in Run 20 was effective in preventing sodium leakage from the crucible. To allow use at higher temperatures (melting point of silver chloride is 455 C), silver chloride was impregnated on coconut charcoal and tested up to 900 C (Runs 36 and 37). Little or no bed caking occurred. Similarly, copper chloride has been impregnated on both activated carbon and coconut charcoal with comparable results. The copper chloride and silver chloride-impregnated beds have so far shown some decomposition during the runs. The hottest grains show respectively metallic copper and silver deposits after the runs.

Whereas effective bed materials prevented any sodium from leaking through for the first type of run described above, a trace of sodium leakage occurred with effective materials for all the runs at 900 C and atmospheric pressure, i.e., second type. A trace amount for these data is one that gives a positive flame test but an insufficient amount for routine analysis. The lower limit of the analytical method used is 1 mg of sodium and this corresponds to about 1/1000 of the sodium charged, or 0.1 per cent.

For comparison, the refractory alumina bed of Run 28, although taken only as high as 700 C, allowed at least ten times as much sodium to leak through the bed as in comparable runs made with sorbent beds at 900 C.

Runs 23 and 35 illustrate the effect of temperature drop across the bed in sodium retention. Both were made with a bead type activated alumina. In Run 23 sodium leakage occurred when no temperature drop existed whereas in Run 35 no sodium leakage occurred for a temperature drop of from 420 C at the bottom to about 250 C at the top. The crucible temperatures shown are the same as the bottom bed temperatures.

All runs except one were made with sodium as the typical alkali metal. Run 18 was made with cesium. No difference in bed performance was apparent.

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The tests so far have shown that at least 99 per cent of vaporized alkali metals can be stopped by a relatively shallow bed. In the next quarter, the effect of bed temperature and the capacity of the most promising materials will be more closely determined.

6. Removal of Noble Metals from Uranium

(J. B. Knighton,* V. N. Thelen)

The noble metals, ruthenium, rhodium, palladium, molybdenum, and presumably technetium, are not removed by the oxide slagging process. One of the ways in which the concentrations of these materials can be controlled in recycled fuel is by physical removal of a small portion of the fuel (drag-out) and replacement with fresh fissionable material. If the major fissionable constituent is plutonium, there is the possibility that a small fraction of the core material can be cycled through the magnesium extraction process, which separates plutonium from some of these noble metals. This would eliminate the necessity for physical drag-out of some core material. No alternative to physical drag-out is presently available if the fissionable material is uranium-235. Scouting experiments are presently being performed on solutions of uranium-noble metal alloys in metals such as zinc to determine if by fractional crystallization procedures, separations of uranium and noble metals can be effected. Previous work along this line has been reported by S. Isserow.²¹

The uranium-zinc system has a two-phase region on the zinc-rich portion of the phase diagram in which there is (1) solid uranium-zinc intermetallic compound (UZn_9) and (2) liquid zinc-uranium alloy (α) as shown in Figure 27.

FIGURE 27

SCHEMATIC URANIUM ZINC PHASE DIAGRAM

*Special Scientific Employee on loan from American Smelting and Refining Company.

²¹Isserow, S., MIT-1117, Technical Progress Report for the Period March 1954 Through June 1954.

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The objective of this work is to use these properties to make a separation between uranium and the noble metal fission product impurities by (1) making a homogeneous one-phase solution with uranium and zinc, (2) controlled cooling to crystallize UZn_9 , leaving the noble metal impurities in the liquid phase, and (3) making a physical separation of the uranium-rich solid phase from the noble metal-rich liquid phase.

A run has been made to determine the solubility versus temperature curve for ruthenium in zinc. Likewise, a run using a uranium-ruthenium alloy has been made to determine if uranium will crystallize out preferentially to ruthenium. Analytical results for these runs are not yet available.

Metallographic examination of polished and etched ingots has revealed that uranium and ruthenium form independent compounds with zinc. The ruthenium-zinc compound is identified by its black color and angular shape; when etched, there is pronounced galvanic cell action between the crystal and the zinc matrix, which results in preferential dissolution of the zinc around each crystal. The uranium-zinc intermetallic compound (UZn_9) forms dendrites of leafy tree-like crystals with a characteristic bronze color.

Metallographic examinations also show that under controlled cooling, the UZn_9 crystallizes out first and segregates to the bottom of the crucible. Some ruthenium-zinc crystals are associated with this UZn_9 . A layer of ruthenium-zinc crystals settles out on top of the UZn_9 -enriched layer.

Preliminary runs have shown that the above-mentioned segregation may be accentuated if magnesium is added to the uranium-zinc melt. Additional work is planned in this direction.

7. Extraction of Plutonium by Liquid Magnesium
(I. O. Winsch, W. H. Spicer, A. Cole,* K. Olsen**)

Work was continued in the semi-works on studies of the extraction of plutonium from molten uranium with molten magnesium, and on the development of equipment for the extraction and the subsequent distillation steps. A five-kilogram-scale batch extraction unit has been installed and preliminary testing begun. A second magnesium distillation unit has also been received and will be tested in the next quarter.

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****Student Aide.**

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a. Magnesium Extraction Studies1. Successive Magnesium Extractions of One Per Cent Plutonium Alloy

Four successive, 1/2-hour, batch magnesium extractions were made of a 500-gram charge of a uranium-chromium alloy (5 w/o chromium) which initially contained 1 w/o plutonium. Between 300 and 400 grams of magnesium were used for each contact. Slightly more than 85 per cent of the plutonium was extracted in the magnesium phases (Table 50). The over-all plutonium material balance was 96 per cent.

Table 50

SUCCESSIVE BATCH EXTRACTION OF
PLUTONIUM WITH MAGNESIUM

(Equipment description on page 122, ANL-5602)

Uranium Alloy: 5 w/o chromium, 1 w/o plutonium
Charge: 500 g of alloy, 5.17 g of plutonium
Extraction Time: 1/2 hour

Extraction No.	Wt of Mg Used, gm	Plutonium in Extract		Mole Fraction Ratio ^a
		wt, gm	% of Available Pu Extracted	
1	347	2.91	56.5	0.185
2	324	0.86	38.5	0.095
3	399	0.45	32.2	0.059
4	355	0.18	19.0	0.046
Total		4.40		

^aMole fraction of plutonium in magnesium phase to that in uranium phase. At equilibrium, the ratio should be 0.21.

In these extractions the ratio of the mole fraction of plutonium in the magnesium phase to that in the uranium phase decreased from 0.185 to 0.046. Data from this laboratory (see page 110) and from Atomics International for plutonium concentrations ranging from a few parts per million to 1 w/o indicate that at equilibrium this ratio should be about 0.21. Failure to achieve this ratio may be due to several causes, such as (1) failure to achieve equilibrium, (2) formation of inextractible plutonium compounds (such as the oxide or intermetallic compounds) with impurities, and (3) presence of an inextractible alpha emitter other than

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plutonium. A pulse analysis of alpha emissions from a sample of the final uranium phase has been made to check this latter possibility. About 2 per cent of the total alpha emissions were due to the combination, americium-241 plus plutonium-238. Since this is about the amount of plutonium-238 which is usually present, it is believed that little of the alpha activity is due to americium.

2. Five-Kilogram-Scale Batch Extraction Unit

Installation of a five-kilogram-scale extraction system was completed late last quarter. The system is composed of an extraction vessel, a magnesium charge vessel, and receivers for the separated magnesium and uranium phases (see Figures 28 and 29). It is intended with this unit to obtain experience in handling the molten metal phases (transfer, mixing, and separation) and to conduct plutonium extractions at full scale plutonium levels (1 w/o). The phases will be transferred from vessel to vessel by means of pressure and vacuum. All transfer lines are fabricated of tantalum which is backed up with stainless steel outside the vessels to prevent oxidation of the tantalum. The entire unit is positioned within a 20-kw resistance furnace capable of maintaining temperatures of 1000 C. About five hours are required to heat to 1000 C, and 24 hours to cool to room temperature.

Magnesium has been successfully transferred from the charge vessel to the extraction vessel and agitated therein for one-half hour. Further transfer to the magnesium and uranium receivers resulted in overflowing the uranium receiver, so that considerable difficulty was experienced in removing this vessel. Because of the experience gained in this first test, a pressure equalizing system is being installed to provide more effective control of the transfer operations. It may also be necessary to employ "freeze" valves between the vessels. Development of liquid level alarms and methods of liquid level determinations is to be undertaken.

b. Magnesium Distillation

The magnesium distillation apparatus has been modified to provide a sodium-cooled condenser. This apparatus will be tested in the next quarter.

8. Inert Gas Purification

(A. A. Chilenskas, D. D. Busch, P. Kelsheimer)

Work was continued on the development of procedures for removing oxygen and nitrogen from the inert argon blanketing gas for a pyrometallurgical processing facility.

FIGURE 28

PHOTOGRAPH OF FIVE-KILOGRAM-SCALE
MAGNESIUM EXTRACTION UNIT

FIGURE 29.

FIVE-KILOGRAM SCALE MAGNESIUM
EXTRACTION UNIT. (Schematic)
(Unit is installed in large resistance furnace)

a. Removal of Oxygen from Argon by Conversion to Water and Subsequent Drying

A process for removing oxygen from argon by catalytically combining it with a metered stoichiometric quantity of hydrogen has been described in ANL-5560, page 106. The water is subsequently removed in a drier. In the past quarter, it was found possible to sorb hydrogen upon the catalyst (a palladium catalyst, 0.5 wt per cent on alumina) previous to use so that it was available to react with oxygen in the gas stream. This would eliminate the close control required by the titration procedure. However, a combination of the titration and sorption procedures might be advantageous in prolonging the time before catalyst regeneration.

The absorptive capacity of the 0.5 per cent palladium catalyst was determined using the apparatus shown schematically in Figure 30.

FIGURE 30

SCHEMATIC OF APPARATUS USED FOR DETERMINING CATALYST
ABSORPTIVE CAPACITY

The capacity of the catalyst for hydrogen was determined in two ways:

- (1) By passing oxygen through a hydrogenated catalyst bed (150 ml superficial volume) until oxygen breakthrough occurred. Under the experimental conditions employed, a space velocity of 400 hr^{-1} * and an oxygen concentration of 2200 ppm, complete conversion of oxygen to water was effected until the oxygen breakthrough occurred. The amount of available hydrogen determined by these measurements was 70.5 ml or 0.47 ml/ml of catalyst.

$$\text{*Space velocity} = \frac{\text{volumetric gas flow at STP}}{\text{volume occupied by getter}}$$

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- (2) By passing at a known rate hydrogen in an argon stream (1 per cent hydrogen) through a catalyst, which had been previously treated with oxygen to burn off all available hydrogen, until hydrogen breakthrough occurred. The hydrogen sorbed was 95.1 ml, which is somewhat higher than the available hydrogen determined by oxygen breakthrough measurement. No detectable breakthrough of hydrogen occurred until the catalyst was loaded to essentially 100 per cent capacity.

In both of the above cases, the time for breakthrough of hydrogen or oxygen to occur was a factor of 8 to 10 greater than the equipment response time, the time required for oxygen or hydrogen to be detected by the dew point meter with the hydrogenation catalyst by-passed.

b. The Use of Hot Copper as an Oxygen Getter

The use of copper as a getter for oxygen is fairly common, but the literature concerning its use is mainly descriptive. Consequently, it was felt desirable to perform several experiments to evaluate the efficacy of hot copper for the removal of oxygen from argon.

The apparatus is shown schematically in Figure 31. The getter used was fine copper shot (Mallinckrodt, reagent grade) screened between 10 and 20 US standard mesh. The weight of shot charged was 73.13 g and the volume occupied was 15 ml. The mean diameter of a random sampling (26 measurements) was 0.058 inch.

FIGURE 31

EQUIPMENT USED TO DETERMINE EFFICIENCY OF COPPER AS AN OXYGEN GETTER

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The gettering efficiency of the copper was tested at 600 C with an influent stream of argon containing about 1000 ppm oxygen by continuously monitoring the effluent stream with a dew point recorder. The effluent oxygen is converted to moisture by the use of a 0.5 per cent palladium catalyst and excess hydrogen. The results of the tests made are given in Table 51.

Table 51

USE OF HOT COPPER AS AN OXYGEN GETTER
(See details of copper furnace in Figure 31)

Copper Getter Temp: 600 C

Run No.	Gas Flow			Inlet O ₂ Conc (ppm)	Effluent Oxygen Conc (ppm) After Indicated Time (min)					Final Cu _b Burnup (%)
	(ml/min)	Space Vel (hr ⁻¹) ^a	Superficial Vel (ft/sec)		0	20	60	90	120	
1	500	1336	0.22	1015	0	1	2→(end of test)			0.214
2	500	1336	0.22	1015	0		3		6	0.428
3	1000	2672	0.44	1110	0	2	25	61	112	0.89
4	1000	2672	0.44	1110	0	0	0	1	44	0.93

^aSpace velocity = $\frac{\text{volumetric gas flow at STP}}{\text{volume occupied by getter}}$

^bCalculated as per cent of copper charge converted to CuO.

As shown in Run 2, the getter efficiency is >99 per cent up to a burn-up of at least 0.43 per cent for a space velocity of 1336 hr⁻¹. Doubling the gas rate resulted in some oxygen breakthrough before 0.43 per cent burn-up in Run 3. However, after regeneration of the catalyst, no oxygen breakthrough occurred until about 0.7 per cent burn-up (Run 4). The increase in getter activity is believed to be due to the hydrogen regeneration of the getter in that the surface of the shot was completely changed from a shiny smooth appearance to a dull, irregular appearance. The extent of reaction in Runs 1 and 2 was not sufficient to give this changed condition over the entire surface of the getter. However, the effect of many operating and regeneration cycles on the copper activity and appearance is not known. The loss of getter activity with the formation of an oxide skin is apparent in these runs, especially Runs 3 and 4.

Regeneration of the copper was accomplished in times of the order of 1 to 1½ hours by passing argon containing 0.5 per cent hydrogen over the getter at a temperature of 400 C.

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It appears that satisfactory oxygen removal from argon with copper at 600 C is possible by operating at low getter burn-up (<0.5 per cent). Reasonably high gas flow rates are permissible.

c. Nitrogen Removal from Argon

Work was continued on the investigation of methods for removing nitrogen from argon. As pointed out in the previous quarterly, it is not certain that nitrogen removal by chemical means is necessary, since the nitrogen concentration in the argon can apparently be high enough (5 per cent and perhaps greater) that simple purging with pure argon is the most economical procedure. However, some work on chemically removing nitrogen (mainly by using hot calcium as a getter) has been done to provide for the possibility that lower nitrogen concentrations in the argon blanketing gas may be desirable.

1. Use of Hot Calcium as a Nitrogen Getter

It has been reported by a German investigator²² that the reactivity of calcium with nitrogen is inhibited by the formation of a calcium nitride skin during the initial exposure and that sodium metal present in small quantities will prevent the inhibiting effect of the skin formation. The rate of reaction between calcium and nitrogen is also reported as being a maximum at 400 to 440 C. However, this latter observation appears to be based upon a reaction which has progressed sufficiently far that the character of the nitride product has changed from an adherent protective film to a more porous crystalline structure. In the United States and Great Britain, nitrogen gettering with calcium alone is often carried out at a temperature of 650 C.

In order to evaluate these alternative conditions, tests were made in a closed system to study the activation of calcium by sodium, the effect of operation at temperatures of 440 C and 650 C using calcium and sodium-activated calcium, and the effect of the extent of calcium burn-up upon the activity of sodium-activated calcium.

The apparatus used for these experiments is shown in Figure 32. The getter charge, weighing approximately 3 grams, consisted of 5 ml of calcium or calcium-sodium alloy (5 per cent sodium) and was screened between 10 and 30 US standard sieves. The temperature of the getter was measured by an internally located chromel-alumel thermocouple. In order to sodium-activate the calcium, one or two lumps of sodium metal, weighing approximately 0.2 gram, were added with the calcium.

²² von Antropoff, A., The Kinetics of the Reaction Between Calcium and Nitrogen, Z. Phys. Chem., 137, 209-237 (1928).

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FIGURE 32

EQUIPMENT USED TO STUDY REMOVAL OF
NITROGEN FROM ARGON

To determine the activity of a getter, the apparatus was charged with argon and nitrogen and the gases mixed by back and forth gas displacement from the burette to the gas reservoir. The getter was heated to the desired operating temperature with the gas initially at atmospheric pressure and pumped through the getter. After the desired number of pumping cycles, the heater was cut off, and the entire apparatus permitted to cool to room temperature. The decrease in volume measured with the system gas at room temperature and at atmospheric pressure represented the amount of nitrogen absorbed by the getter.

The results of the various runs are given in Table 52. The following points may be noted:

- (1) The effect of sodium, present in an alloy or added as lump, has a marked effect on the activity of calcium. Reaction rates at 440 C are comparable to those for pure calcium at 650 C (compare Runs 4, 13, 14, and 15 with Run 11).
- (2) Once a calcium-sodium alloy has been heated to 650 C, the beneficial effect of sodium is greatly diminished or lost and the material is no longer an effective getter at 440 C (see Runs 7a, 9, and 10 made following such a treatment).
- (3) Pure calcium is an effective getter at temperatures of 650 C.

The major effect of sodium is that it provides efficient gettering of nitrogen at a considerably lower temperature than is possible with pure calcium. It is noteworthy that through Runs 13, 14, and 15, the lump sodium-activated getter underwent a 9 per cent burn-up without any detectable change in activity.

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Table 52

NITROGEN REMOVAL BY CALCIUM AND SODIUM-ACTIVATED CALCIUM
(See apparatus in Figure 32)

Total gas volume = 90 ml

Run No.	Getter No.	Getter Type	Getter Temp (C)	Initial N ₂ Conc (Vol %)	Per Cent of Total Nitrogen Absorbed			
					Heatup ^a	2 Cycles ^b	6 Cycles ^b	14 Cycles ^b
4	1	Calcium-Sodium Alloy	440	14.8	19.5	67.8	88.2	98.4
5	1	Calcium-Sodium Alloy	650	20.5	38.6	80.7	97.3	-
6	1	Calcium-Sodium Alloy	650	15.7	17.8	86.4	97.4	-
7a ^c	1	Calcium-Sodium Alloy	440	22.0	0	0	0	-
7b	1	Calcium-Sodium Alloy	650	22.0	11.1	77.2	95.3	99.4
8	2	Calcium-Sodium Alloy	650	14.2	11.7	83.5	95.2	98.1
9 ^c	2	Calcium-Sodium Alloy	440	15.5	8.9	23.9	31.9	39.9
10 ^c	2	Calcium-Sodium Alloy	440	14.4	0.9	2.7	-	5.4
11	3	Calcium	440	15.3	0.75	3.0	-	-
11	3	Calcium	650	14.9	21.0	83.5	94.0	94.7
13	4	Calcium + Lump Sodium	440	16.2	24.3	89.0	98.5	100.0
14	4	Calcium + Lump Sodium	440	15.9	24.1	86.5	97.0	-
15	4	Calcium + Lump Sodium	440	30.9	17.3	82.3	98.2	-

^aThe nitrogen absorbed when the getter is heated to the operating temperature and quickly cooled without pumping any gas through the getter.

^bA cycle refers to the displacement of the gas through the getter to a reservoir and back again in one minute.

^cOnce the calcium-sodium alloy has been heated to 650 C, it is no longer an effective getter at 440 C.

Two runs were made with lump sodium-activated calcium at 440 C in which the getter was entirely converted to the nitride (Table 53). It can be seen that after about 40 per cent calcium burn-up the rate of reaction fell to less than half the initial value and continued to diminish to zero as 100 per cent burn-up was approached. Other investigators²³ have found that 20 to 30 per cent conversion (calcium at 650 to 700 C) can be achieved initially, but that a further conversion of 20 to 25 per cent could be obtained after cooling to room temperature. Since in the above two runs, the getter charge was thermally cycled many times, it is not known whether the thermal cycling or the use of a sodium activator had the biggest effect. Continuous flow experiments planned for the next quarter will resolve this question.

²³Pawson, R. L., Argon Purification for Metallurgical Operation - AWRE-0-16/54

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Table 53

EFFECTIVENESS OF SODIUM-ACTIVATED CALCIUM
FOR NITROGEN GETTERING AS A FUNCTION
OF CALCIUM BURN-UP

Temp: 440 C

N₂ Conc: 37 to 40 per cent by volume in argon

Per Cent Calcium Burn-Up	Per Cent Nitrogen Removed per Cycle ^a	
	Run 16	Run 17
0	14.0	14.5
45	3.5	6.5
72	3.0	7.0
95	1.0	2.0

^a Displacement of gas from burette to gas reservoir and back in one minute.

The use of two other materials, aluminum and magnesium, which reportedly form nitrides and are cheaper than calcium was tested. Aluminum with lump sodium and sodium fluoride (the latter has also been reported as a metal activator²⁴) was tested at 600 C, but no reaction with nitrogen occurred. Nor was there reaction at 500 C with magnesium in the presence of a small amount of lump sodium, but increasing the temperature to 600 C instigated the reaction with nitrogen.

It appears from these data that a process for the removal of nitrogen from argon using sodium-activated calcium may be feasible at about 450 C. If essentially 100 per cent burn-up is desired, a moving-bed type apparatus may be necessary in which calcium and sodium are fed at one end and the nitride discharged at the other.

In the next quarter, the study of nitrogen gettering in a flow system will be studied using sodium-activated calcium at 440 and 650 C to compare the efficacy of activated calcium at these two temperatures and to determine the role of thermal cycling in the achieving of complete calcium burn-up.

²⁴ Ephraim, F., Inorganic Chemistry, 4th Edition, page 630 (1946)

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VI. ANALYTICAL RESEARCH AND SERVICES

A. X-Ray Spectrometric Determination of Plutonium in Solution

(D. S. Flikkema, R. Schablaske)

An X-ray spectrometric method is being developed for rapid, convenient determination of plutonium in the concentration range 3 to 9×10^{-3} M. One-half ml of solution is used for each determination so that the total plutonium requirement is between 0.35 and 1 mg. Counting times range from two to four minutes.

Analysis by this physical method is attractive for several other reasons. Since X-ray emission is independent of the valence state of the emitting atoms, it removes this factor from concern, a feature which is particularly desirable for elements such as plutonium whose chemistry is complex because of many possible valence states in solution. Further, the adaptability of X-ray spectrometry to routine analysis of liquid samples has been demonstrated with a similar method for uranium (ANL-5529).

1. Apparatus

The X-ray equipment used in this work is the basic Norelco (North American Philips Company) diffractometer with spectrograph accessories. Primary X radiation is provided by a Norelco FA-60 tungsten target tube which is operated at 57 kilovolts peak and 47 milliamperes. The fluorescent beam defined by an open source-collimator tube is diffracted from a lithium fluoride analyzing crystal whose "d" is 2.014 angstroms. This diffracted radiation is collimated with a set of parallel plates, four inches long spaced 0.005 inch apart (ratio 800 to 1), and the remaining, almost parallel rays are detected with a halogen-quenched Geiger tube. Counting is done with the Geiger tube positioned at a two-theta value of 24.91 degrees, the angular location of the plutonium $L\alpha_1$ emission line for the lithium fluoride analyzer.

Instrumental modifications necessary to decrease fluctuations in the primary X-ray intensity and in the counter tube operating voltage are described in ANL-5529, page 122.

The all-glass sample cell currently being used in this study is similar in construction to, but smaller in dimensions than, that employed for uranium analyses (ANL-5529). Its diameter is 8 mm, height 7 mm, capacity including side-arms 1/2 ml, and window thickness 0.075 mm. The cell rests within an aluminum dish large enough to contain the sample should the cell crack or break.

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2. Procedure and Results

Three solutions - 2.59 , 6.48 and 9.72×10^{-3} M plutonium in 1 M hydrochloric acid - were prepared by gently evaporating aliquots of a plutonium stock solution (6.48×10^{-3} M in 6 M hydrochloric acid) to dryness under a heat lamp and then taking up the residue to the desired concentration with 1 M hydrochloric acid. A series of count rates were determined with aliquots from these three solutions and from a 1 M hydrochloric acid "blank." The recorded variable in each determination was the time required to register 64,000 total counts. The data are summarized in Table 54 and shown graphically in Figure 33, with count rates both uncorrected and corrected for Geiger counter resolving time of 270 microseconds.

Table 54

PLUTONIUM CONCENTRATION IN 1 M HCl SOLUTION
VS. COUNT RATE AT 57 KVP AND 47 MA

Pu Molarity ($\times 10^3$)	Average Time for 64,000 Counts ^a	Count Rate (uncorrected for counter resolution)	Count Rate (corrected for counter resolution)	Fraction of Total Counts Due to Pu (uncorrected)
0	343.4 ± 1.0 sec	186 c/sec	196 c/sec	-
2.59	239.7 ± 0.4 sec	267 c/sec	288 c/sec	0.30
6.48	171.1 ± 0.3 sec	374 c/sec	416 c/sec	0.50
9.72	140.8 ± 0.2 sec	454 c/sec	517 c/sec	0.59

^aThe error estimate is average deviation.

FIGURE 33

TYPICAL CALIBRATION CURVE FOR THE X-RAY SPECTROMETRIC
DETERMINATION OF PLUTONIUM IN SOLUTION

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3. Discussion

The characteristics of secondary X-ray emission and primary radiation scatter from a plutonium solution under the conditions of this study are shown by the linear ratemeter scan reproduced as Figure 34. It also illustrates factors, such as signal to noise ratio, which determine the choice of the emission line whose intensity is correlated with element concentration for the basis of the method.

FIGURE 34

X-RAY SPECTROGRAM OF A
 $9.7 \times 10^{-3} \text{ M}$ Pu SOLUTION
 IN 1 M HCl
 (LiF analyzing crystal)

Table 55 gives an idea of the reliability found in preliminary results under the conditions selected and permits comparison with the statistical deviations expected from the 64,000 total counts accumulated in each determination. The indicated reliability does not include manipulation errors, since the data are from triplicate sampling of a single solution at the given concentration. As yet there are too few results for very meaningful assessment of errors, but to ameliorate this lack the sum of deviation squares was divided by $(n-1)$, instead of n , results. The expected deviation of the plutonium result is calculated, as usual, from the square root of the sum of the squares of the deviations of the total count and the background count which would have been accumulated in the same period. Reducing this deviation by counting for a longer interval to accumulate

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Table 55

RELIABILITY OF PRELIMINARY RESULTS FOR PLUTONIUM
IN SOLUTION BY X-RAY SPECTROMETRY

Pu Molarity ($\times 10^3$)	Number of Results	Per Cent Standard Deviation	
		Calculated From Results	Calculated From Counting Statistics
2.59	3	1.2	1.7
6.48	3	0.6	1.0
9.72	3	0.5	0.8

more than 64,000 counts is limited by incipient bubble formation in the sample cell after four minutes residence in the spectrometer. The alternative of improving signal to noise ratio has other obvious advantages as well, and is being approached in several ways, including reduction of primary radiation scatter and discrimination against the background with energy selective detectors.

Matrix effects are being examined to assess the effect of solvent acid concentration on the plutonium line intensity as well as the error contribution of likely interferences.

B. Energy-Selective Detectors to Solve Background Problems in X-Ray Spectrometry

(D. S. Flikkema, R. V. Schablaske)

A widely experienced problem in quantitative analysis by X-ray spectrometry arises from high coherent and incoherent (Compton) scatter of X radiation incident on the sample, sample housing, and other surfaces. It is this diffuse scatter of continuum, as differentiated from Bragg scattering of characteristic radiation by an analyzing crystal, which at present sets the lower limit of usefulness for our spectrometric methods. In particular, this is the case with aqueous samples, since the amount of diffuse scatter is inversely related to the atomic number of the scattering atom. To reduce such background counts and thus to improve analytical sensitivity and reliability, detectors can be used which discriminate energetically in various ways among X-ray photons. During recent years improvements in proportional and scintillation counters and in the associated circuitry have made electronic discrimination the most effective and generally useful approach.

We have modified a Norelco (North American Philips Company) X-ray spectrometer for counting with either a proportional-type or a sodium iodide-thallium activated scintillation detector, whichever is the

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detector of choice for a specific analytical situation. The proportional counter pulse is pre-amplified by means of a stabilized circuit immediately adjacent to the counter tube. On the other hand, the scintillator pulse is large enough so that only a cathode follower is used with this counter. Amplification is provided by the highly flexible Oak Ridge model AID linear amplifier,* and pulse differentiation by the Oak Ridge model No. 5Q-1192 single channel differential analyzer.* The Norelco binary stage scaler is preceded by a fast decade stage resolving at about one microsecond, and count registering is done electronically by an assembly of three glow tubes with switching for total 10, total 100, and total 1000. The original 0 to 6000-second interval timer was replaced with a 0 to 1000-second timer which proved to be reliable to ± 0.05 second when calibrated.

C. Direct Assay of Molybdenum and Ruthenium in Ternary Alloys With Uranium by X-Ray Emission
(D. S. Flikkema, R. V. Schablaske)

Additional non-radioactive alloys representative of high burn-up reactor fuels have been obtained and examined in order to define more carefully some of the factors in the X-ray spectral method for molybdenum and ruthenium in a uranium matrix (ANL-5560, pages 128 to 134).

The range of the alloys examined now covers 0.7 to 5.8 weight per cent molybdenum and 0.5 to 4.6 weight per cent ruthenium. In this range the average absolute error of all the results for molybdenum is 0.03 per cent, with the maximum not exceeding 0.08 per cent, and for ruthenium 0.05 per cent with the maximum absolute error not exceeding 0.11 per cent. This order of reliability is manifest without correcting the line intensities in any way other than subtracting background. Indeed it appears that the working curve for molybdenum analyses between 1.5 and 5 per cent can be established well enough for relative reliability of ± 2 per cent with only two well-standardized alloys at the extremes of this range.

The line intensities given in counts per second in Tables 56 and 57 were obtained under conditions similar to those previously reported with the exception that the tungsten target primary tube was operated at 60 kilovolts peak and 50 milliamperes for improved signal to background ratios. Figures 35 and 36 are calibration plots of intensities in counts per second versus chemically determined weight percentages, representing the data of Tables 56 and 57.

A series of alloys, designated SNY in the tables, was prepared** to begin a study of the effect of varying molybdenum on the line intensity from fixed ruthenium concentration. The data at 0.5 weight per cent ruthenium, listed separately in Table 58, show a discernible ruthenium intensity

*Commercially available from Radiation Counter Laboratories.

**We are indebted to Frank L. Yaggee of the ANL Metallurgy Division for the alloys.

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Table 56

CALIBRATION DATA IN TERMS OF X-RAY LINE INTENSITY VS WEIGHT PER CENT
OF MOLYBDENUM IN TERNARY ALLOYS WITH URANIUM

Specimen	Weight Per Cent by Chemical Analysis		Line Intensity at 30.35° 2θ (128,000 counts taken) MoKα + ULβ ₃ + background ^a	Weight Per Cent Mo from Calibration Curve	Error	Relative Error
	Mo	Ru				
Unalloyed uranium	-	-	474 c/sec	-	-	-
1E	0.71 ₆	0.88 ₃	602	0.77	+0.05 ₄	+7.5%
4E	0.91 ₅	1.90	626	0.92	+0.00 ₅	+0.5
4EAA	0.91 ₃	1.88	626	0.92	-0.00 ₇	+0.8
SNY27A	1.02	0.49 ₈	634	0.97	-0.05	-4.9
SNY27B	0.98	0.50 ₁	636	0.98	0.0	0.0
2E	1.32	1.54	697	1.37	+0.05	+3.8
2EAA	1.27	1.60	687	1.30 ₅	+0.03 ₅	+2.8
2EAB	1.29	1.49	688	1.31 ₃	+0.02 ₃	+1.8
3E	1.55	0.81 ₇	721	1.52 ₈	-0.02 ₂	-1.4
8EAA	1.64	4.21	739	1.64 ₅	+0.00 ₅	+0.3
8EAB	1.72	4.07	746	1.69	-0.03	-1.7
11E	3.21	4.62	965	3.23	+0.02	+0.6
16E	3.79	3.13	1036	3.77	-0.02	-0.5
SNY26A	4.06	0.49 ₈	1065	3.99 ₅	-0.06 ₅	-1.6
SNY26B	3.93	0.49 ₆	1064	3.99	+0.06	+1.5
SNY25A	4.93	0.48 ₄	1205	5.01	+0.08	+1.6
SNY25B	5.03	0.49 ₃	1199	4.98	-0.05	-1.0
15EAA	5.73	2.68	1321	5.77 ₅	+0.04 ₅	+0.8
15EAB	5.77	2.64	1315	5.73 ₅	-0.03 ₅	-0.6
				Average	0.03 ₄	

^aThe intensity at 30.35 minus the intensity from unalloyed uranium at 30.35 is taken as the molybdenum contribution to the intensity at this angle.

Table 57

CALIBRATION DATA IN TERMS OF X-RAY LINE INTENSITY VS WEIGHT PER CENT
OF RUTHENIUM IN TERNARY ALLOYS WITH URANIUM

Specimen	Weight Per Cent by Chemical Analysis		Line Intensity at 27.47° 2θ (64,000 counts taken)	Weight Per Cent Ru from Calibration Curve	Error	Relative Error
	Ru	Mo				
Unalloyed uranium	-	-	90 c/sec	-	-	-
SNY27A	0.49 ₈	1.02	164	0.47	-0.02 ₈	-5.6%
SNY27B	0.50 ₁	0.98	164	0.47	-0.03 ₁	-6.2
SNY26A	0.49 ₈	4.06	170	0.50 ₅	+0.00 ₇	+1.4
SNY26B	0.49 ₆	3.93	170	0.50 ₅	+0.00 ₉	+1.8
SNY25A	0.48 ₄	4.93	170	0.50 ₅	+0.02 ₁	+4.3
SNY25B	0.49 ₃	5.03	172	0.52	+0.02 ₇	+5.5
3E	0.81 ₇	1.55	215	0.80 ₃	-0.01 ₄	-1.7
1E	0.88 ₃	0.71 ₆	216	0.81	-0.07 ₃	-8.3
2E	1.54	1.32	334	1.61	+0.07	+4.5
2EAA	1.60	1.27	331	1.59	-0.01	-0.6
2EAB	1.49	1.29	329	1.57 ₅	+0.08 ₅	+5.7
4E	1.90	0.91 ₅	361	1.79 ₇	-0.10 ₃	-5.4
4EAA	1.88	0.91 ₃	363	1.81 ₃	-0.06 ₈	-3.6
15EAA	2.68	5.73	486	2.71	+0.03	+1.1
15EAB	2.64	5.77	487	2.71 ₅	+0.07 ₅	+2.8
16E	3.13	3.79	531	3.05 ₅	-0.07 ₅	-2.4
8E	4.17	1.85	661	4.13 ₅	-0.03 ₅	-0.8
8EAA	4.21	1.64	666	4.18	-0.03	-0.7
8EAB	4.07	1.72	665	4.17	+0.10	+2.5
11E	4.62	3.21	700	4.51	-0.11	-2.4
				Average	0.05 ₀	

^aThe intensity at 27.47 minus that from unalloyed uranium at 27.47 is taken as the ruthenium intensity.

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FIGURE 35

TYPICAL PLOT OF X-RAY INTENSITY VS. WEIGHT PERCENTAGE FOR THE DIRECT ASSAY
OF MOLYBDENUM IN TERNARY ALLOYS WITH URANIUM

FIGURE 36

TYPICAL PLOT OF X-RAY INTENSITY VS. WEIGHT PERCENTAGE FOR THE
DIRECT ASSAY OF RUTHENIUM IN TERNARY ALLOYS WITH URANIUM

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Table 58

EFFECT OF VARYING MOLYBDENUM ON THE LINE INTENSITY FROM
FIXED RUTHENIUM CONCENTRATION IN TERNARY ALLOYS

Specimen	Weight Per Cent (by Chemical Analysis)		RuK α Intensity (from 64,000 counts at 27.47 2θ)
	Ru	Mo	
Unalloyed uranium	-	-	90 c/sec
SNY27A	0.49 ₈	1.02	164
SNY27B	0.50 ₁	0.98	164
SNY26A	0.49 ₈	4.06	170
SNY26B	0.49 ₆	3.93	170
SNY25A	0.48 ₄	4.93	170
SNY25B	0.49 ₃	5.03	172

increase of about 1.2 per cent per unit increase in weight per cent molybdenum, or, alternatively, decrease in weight per cent uranium. The same type of effect, due to lowering of the mass absorption of the matrix when uranium atoms are replaced by less absorbing atoms, can be found in the fact that the line intensities corrected for expected coincidence losses in the Geiger detector depart much further from being linear with concentration than do the uncorrected count rates. In fact, an expanded version of the calibration plot for the more extensive molybdenum data (Figure 36) seems to be sigmoid, with the decrease in matrix absorption beginning to over-compensate for counter losses in the concentration region beyond four to five per cent molybdenum.

It is noteworthy that the SNY alloys are essentially ternaries but, having been made from a master fissium alloy, they contain palladium, rhodium and zirconium at approximately 0.1, 0.2 and 0.1 weight per cent. At these levels in a uranium matrix and under the conditions of the method palladium is clearly detectable, zirconium only with difficulty because of interference by a weak uranium line ($L\beta_6$), and rhodium not at all since it is masked by the uranium $L\gamma_1$.

To learn the degree of finish which must be given the surface of the alloy slice, the observations tabulated in Table 59 were made. Obviously, smoothness beyond that achieved with 127-micron or 60-micron silicon carbide paper is unnecessary and, with either, the finishing operation is quickly done. Since the data of Table 59 were collected at random times throughout an entire day and since re-locating a given specimen in the plane of its surface was haphazard it can be seen that the stability of our instrument and the in-plane homogeneity of our standard alloys are excellent.

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Table 59

EFFECT OF SURFACE FINISH ON LINE INTENSITY

(41 KVP, 48 MA)

Specimen	Weight Per Cent		Surface Finish	Line Intensity (from 128,000 counts at indicated 2θ angle)	
	Ru	Mo		RuK α	UL β_3 + MoK α
				(27.47)	(30.35)
Unalloyed uranium	-	-	127 micron silicon carbide	43.3 c/sec	228.2 c/sec
			60 micron silicon carbide	43.6	228.3
			22 micron silicon carbide	43.4	229.3
			6 micron diamond paste	43.0	228.7
SNY24	0.52 ₄	2.73	127 micron silicon carbide	79.3	432.9
			60 micron silicon carbide	79.3	432.7
			22 micron silicon carbide	79.8	433.5
			6 micron diamond paste	79.5	431.8
16E	3.13	3.79	127 micron silicon carbide	242.0	518.0
			60 micron silicon carbide	243.4	516.3
			22 micron silicon carbide	242.9	515.3
			6 micron silicon carbide	242.1	518.4

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VII. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste-Processing Operations

(J. Harast, K. Bremer, K. Clark)

There were 58,000 gallons of liquid active wastes collected during the quarter ending September 30 which were processed as follows:

Evaporation	43,000 gal
Concentrator	1,800
Flocculation	13,000
Absorption	50
Solvent Washing	275

B. Gamma-Irradiation Facility(H. G. Swope, J. Harast, A. Rashinskas, L. Marek, R. Thurnblad,
T. Emmering, C. Fremgren)

During the past quarter 3644 samples were irradiated in the gamma-irradiation facility.

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