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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, and September, 1955

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

for July, August, and September, 1955

SUMMARY

I. Direct Cycle Boiling Reactor Entrainment Studies (pages 8 to 10)

The study of entrainment of dissolved radioactivity from a boiling water surface was directed to a study of changes in tracer concentration with time within the boiling liquid. Exploratory laboratory tests were made to study the adsorption of Cs¹³⁷ on stainless steel and pyrex.

II. Solvent Extraction — Study of Dispersion and Coalescence (pages 11 to 13)

Additional data were obtained in developing a correlation between interfacial area of immiscible liquid systems and light transmission. An empirical correlation of interfacial area with physical properties and energy input for stirred systems is being developed.

III. Fluoride Volatilization Separations Processes (pages 14 to 45)

Further data are reported in the development of the fused salt-fluorination process for the processing of zirconium-uranium fuel. When hydrogen fluoride is the fluorinating agent, the rate of hydrogen evolution can be used to monitor the rate of zirconium dissolution. Fluorine, bromine pentafluoride and chlorine trifluoride have been found to be about equally effective as fluorinating agents. In experiments with irradiated material, niobium pentafluoride was carried out of the fused salt melt to the greatest extent of any of the fission products. Further corrosion data are reported.

Apparatus and facilities for preparation and handling of plutonium hexafluoride are complete and a small amount has been prepared.

The gas phase reaction between bromine and bromine trifluoride has been investigated with a successful determination of the equilibrium constant for the formation of bromine monofluoride at 75 C.

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Construction and procurement of equipment for the head end fused salt dissolver to be added to the existing pilot plant is expected to be complete this year.

Process runs in the existing pilot plant equipment using irradiated natural uranium are scheduled for the coming quarter.

IV. Chemical Metallurgical Separations Processes (pages 46 to 77)

Details of performance testing of a new shielded furnace are discussed. Investigations of possible liquid oxides for uranium slagging were continued. A differential thermal analysis apparatus for phase diagram investigations in this field was put in operation. The kinetics of boriding tantalum were investigated. Further evidence of the comparative resistance of tantalum boride to uranium attack is given. Five experiments on plutonium extraction from molten uranium by magnesium were carried out. These gave a mole fraction distribution coefficient of 0.07 ± 0.01 (preliminary value). Uranium powders have been successfully formed and dispersed in and filtered from molten magnesium.

In the semi-works, oxidative slagging runs were conducted with fissionium prepared by dispersing inactive fission products in uranium by powder metallurgy. Analytical results have been obtained to date on only cerium and cesium decontamination. As in tracer fission product level studies, these were removed essentially completely by the oxidative slagging process. On a 2-kg scale, purified ingot yields from fissionium have been around 93 per cent. With fissionium, a fairly bulky and porous slag is formed.

In work related to magnesium extraction of plutonium, the study of magnesium distillation on a 4-kg scale was begun, various extraction devices are being designed for possible testing, and testing of various materials of construction continued.

V. Fluidization Studies (pages 78 to 103)

Work on a continuous fluid-bed process for uranium tetrafluoride production continued. The effect of temperature during reduction and hydrofluorination was studied. Considerable progress was made in the development of a multistage fluid-bed reactor. Further studies on the calcination of wastes were completed.

VI. Reactor Chemistry and Other Problems (pages 104 to 109)

Preparations are underway for the determination of breeding gain in EBR with plutonium loading.

A program is being set up for the systematic study of spontaneous ignitions of uranium, thorium, zirconium and plutonium.

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VII. Analytical Research and Service Work — Solvent Extraction of Molybdenum (pages 110 to 111)

An analytical method for molybdenum by the extraction of the metal xanthate into chloroform was studied.

VIII. Routine Operations (pages 112 to 117)

The gamma irradiation facility has begun operation with the irradiation of 1139 samples during the past quarter. The available irradiation levels are in excess of 10^6 r/hr.

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I. DIRECT CYCLE BOILING REACTOR ENTRAINMENT STUDIES

(A. J. Shor, H. T. Ward*)

The study of the entrainment of dissolved radioactivity from a boiling water surface continued. In addition, attention was directed to the changes in tracer concentration with time within the boiling liquid. These variations resulting from the adsorption of activity on the solid surfaces of the equipment are not only important in explaining the tracer fluctuations in the overhead steam, but are significant in their own right. Exploratory laboratory tests were made to study the adsorption of Cs^{137} on stainless steel and pyrex glass in an effort to establish a quantitative experimental procedure.

Several runs were made in the glass apparatus to follow the change in boiler water concentration. Data previously taken in a stainless steel test loop (ANL-5466, pages 7 to 9; ANL-5422, pages 8 to 16) were examined to determine the extent of adsorption.

An extended run of some fifty hours was made in the glass apparatus in the hope that a steady state condition could be achieved. Results were promising in that the boiler water tracer concentration stabilized fairly well while the overhead counts showed a tendency to level off.

A. Adsorption Tests

Several runs were made in the glass equipment to study the extent of adsorption of the boiler feed water activity during operation.

The equipment used in these studies and the operating conditions have been described previously (ANL-5333, pages 7 to 9, and ANL-5388, pages 7 to 9). Boiler water feed consisted of distilled water of a specific resistance of about 200,000 ohm-cm spiked with Cs^{137} or with Co^{60} while make-up water had a specific resistance of about 500,000 ohm-cm. Hourly samples were taken of the boiler water. Figure 1 shows a graph of the concentration of activity versus time for the runs.

Data taken previously in a stainless steel test loop operating at 600 psia (ANL-5422, pages 12 to 16) were re-examined with particular reference to adsorption of activity. This effect was striking in these runs. About half of the Cs^{137} tracer charged to the unit was adsorbed on the stainless steel in 60 hours of operation.

*On loan from Kansas State College, Department of Chemical Engineering under Participating Institution Program.

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FIGURE 1.

ADSORPTION OF ACTIVITY ON GLASS
BOILER DURING OPERATION.

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B. Entrainment Tests

Several runs were made to investigate the possibility that steady state operation could be obtained by stabilizing the equipment by an extended period of boiling. It was hoped in this way to obtain a stable system for the study of de-entrainment. This technique has been tried with success in boiling heat transfer experiments to improve reproducibility of data. The equipment and conditions of operation were previously reported. It was found that after about 30 hours of operation the decontamination factor, after starting at the beginning of the run with a value of 1.5×10^4 , varied only about ± 10 per cent at a value of 6×10^4 . Operation was interrupted for considerable periods during the run and these interruptions resulted in an abrupt increase in the decontamination factor. During the initial 30 hours, the concentration of activity in the boiler water dropped by a factor of two; thereafter it stabilized fairly well. Discontinuities in the boiler water concentration were not apparent during times of interruptions at which time the boiler remained at room temperature. It is possible that adsorption was too slow at those times to show up as a discontinuity in the curve. Replenishing the make-up water with fresh distilled water reversed the trend of the decontamination factor and caused an abrupt decline in decontamination factor of about 20 per cent. However, the decontamination factor started rising again as the run proceeded further. These data again suggest that the accumulation of dissolved matter in the boiler even at extremely low concentrations either as a result of operation, or standing in a shut-down condition is influential in causing a variation in the entrainment. Furthermore, as evidenced by the change in decontamination factor resulting from a change in make-up water, no real stability had been obtained.

C. Conclusions and Future Plans

Recent work as well as results previously reported have pointed up the difficulty of maintaining stable and predictable conditions with the present system. Evidently, the entrainment arising when boiling high purity water is strongly affected by dissolved impurities accumulated during the boiling. In addition, operation under conditions of low steam velocity (1/2 fps in this case) and therefore relatively low entrainment further aggravates the already strong randomness of the boiling system. Adsorption of the tracer in the boiler leads to further difficulties. To overcome these troubles and to continue to study the present system, i.e., entrainment at low vapor velocities and high liquid purity, a redesign of the present apparatus is required if this approach is to be pursued further.

An effort will be made to assist personnel assigned to Borax-III in determining the amount of activity entrained during operation of the Boiling Reactor.

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II. SOLVENT EXTRACTION — STUDY OF DISPERSION AND COALESCENCE

(W. A. Rodger, V. G. Trice, Jr., J. B. West,*
L. F. Dorsey, D. K. Fleming**)

Work directed toward a fundamental understanding of the processes of dispersion and coalescence in immiscible liquid systems continued. Additional data were obtained in developing the interfacial area--light transmission correlations. A topical report covering this phase of the work is in press and a paper on the subject has been accepted for presentation at the November, 1955, meeting of the American Institute of Chemical Engineers. Considerable progress has been made in developing a correlation of interfacial area with system physical properties and energy input.

A literature survey has been made and a proposal developed for a study of mass transfer using the methods and correlations developed to separate the effects of film coefficients and interfacial area.

A. Determination of Interfacial Area

A number of runs were made to check old data or obtain new data for the interfacial area--light transmittance correlations. These included runs with the following liquids against water: xylene, kerosene, methyl isobutyl ketone, chlorobenzene, methyl isobutyl carbinol, benzene in carbon tetrachloride, benzaldehyde and isoamyl alcohol, and kerosene in methyl alcohol.

A paper¹ and a topical report have been prepared describing the techniques developed for photographically determining the interfacial

*Summer employee from Oklahoma A & M under Participating Institution Program

**Summer employee from Northwestern University under Student Aid Program

¹Trice, V. G., Jr., and Rodger, W. A., "Light Transmittance as a Measure of Interfacial Area in Liquid-Liquid Dispersions"

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area of liquid-liquid dispersions and also presenting a correlation of these areas with the light transmittance through the emulsions. The paper has been accepted for presentation at the November 1955 meeting of the American Institute of Chemical Engineers. The report is in press.

Interfacial area data have been obtained on 17 systems in the six-inch mixing vessel and on three systems in the twelve-inch vessel. Considerable success has been had in developing an empirical correlation of interfacial area with physical properties and energy input. These data will be presented later after the investigation has been extended to the eighteen-inch vessel.

B. Mass Transfer Studies

One very useful application of the light transmittance correlations would be in connection with the development of methods which would facilitate the design of mass transfer equipment in terms of rate in addition to equilibrium concepts. Rate concepts require the evaluation of capacity coefficients which are functions of the interfacial area available for mass transfer.

A survey was made of the literature concerning mass transfer in liquid-liquid systems. It was in the main part restricted to continuous-flow stirred vessels. In most cases it was found that mass transfer data were interpreted in terms of volume-based mass transfer coefficients (k, a). The few exceptions were wetted-wall columns, gently stirred vessels, or similar type equipment in which there was a known fixed amount of interfacial area. In these cases the area-based mass transfer coefficient (k) could be determined. There is considerable advantage to interpretation of data in terms of area-based coefficients because the effect of turbulence due to stirring may be observed separately on the interfacial area (a) and the mass transfer coefficient (k).

On the basis of information gained from the literature survey, a program was initiated to study mass transfer in a stirred vessel in terms of capacity coefficients. The proposed investigation will rely on light transmittance supplemented by photographs to provide a measure of interfacial area.

Some attention has been given to the problem of individually sampling each phase of an oil-water emulsion. Several tests were made involving the use of porous glass discs. These porous glass discs were used to close the ends of two glass tubing sample lines. One disc was treated with an organic silicon compound, "Dri Film", and wet with the oil phase. The other disc was thoroughly cleaned with dichromate cleaning solution and wet with water. When placed in the emulsion, it was found that the disc treated with Dri Film preferentially sampled

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the organic phase while the other disc preferentially sampled the aqueous phase. There was a small amount of cross contamination. However, it appears, after tests with several discs of varying porosities, that with the selection of proper pore size this technique may provide a satisfactory means of independently sampling each phase of an emulsion.

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III. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

Work on the laboratory scale has continued on the development of a fluoride fused salt process for recovering decontaminated uranium from enriched reactor fuels. In order to devise a specific flowsheet upon which head end dissolver design for the existing pilot plant may be based, the principal emphasis continues to be on zirconium-diluted fuels of the STR type. It is expected, however, that this process will be applicable to a wide variety of enriched reactor fuels. The current plan is to immerse the alloy in a fused mixture of sodium and zirconium fluorides at 600 to 700 C and dissolve it by bubbling hydrogen fluoride through the melt. The uranium is then converted to the volatile hexafluoride by bubbling bromine pentafluoride through the melt. This fluorinating agent is used since it is easily condensable, making recycle of the excess fluorinating agent possible. The hexafluoride is then separated and purified by distillation. The laboratory program on enriched reactor fuel processing includes a study of these steps, the application of this type of scheme to other enriched reactor fuels, and appropriate corrosion studies.

Experimental work has indicated that a draft tube increases the dissolution rate and that the rate increases with increasing sparge rate. It has been demonstrated that the rate of hydrogen evolution can be used to monitor the rate of dissolution. Fluorine, bromine pentafluoride and chlorine trifluoride have been compared as fluorinating agents and all found to be about equally effective. Dissolution and fluorination runs with irradiated material have been carried out. Of the fission products, niobium pentafluoride is carried out of the fused salt melt to the greatest extent. The corrosion investigations have continued at 100 C in excess of the expected operating conditions. At present the data show maximum rates for general corrosion of 13 to 20 mils per day and for the sparge tube ends a high value of 87 mils per day. There are indications that the presence of uranium hexafluoride in the sparge gas and simulated corrosion products of nickel accelerate attack slightly, while helium dilution of the sparge reduces the attack slightly. Weldments, in general, appear as good as the parent metal.

Apparatus and facilities for the preparation and handling of plutonium hexafluoride are complete and a small amount has been prepared. This study is orientated toward determination of rates of formation and other factors which may lead to an all-volatility separations process for uranium-plutonium alloys.

The gas phase reaction between bromine and bromine trifluoride has been investigated with a successful determination of the equilibrium constant for the formation of bromine monofluoride at 75 C.

Construction and procurement of equipment for the head end dissolver to be added to the existing pilot plant has proceeded. The additions will permit the semi-works scale recovery decontaminated uranium from STR-type fuel elements. The installation is expected to be complete this year.

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Process runs in the existing pilot plant equipment using irradiated natural uranium are scheduled for the coming quarter.

Exchange of information took place at KAPL with Norval Hawkins on the plutonium hexafluoride program.

A. Laboratory Investigations

1. Enriched Reactor Fuel Processing Studies (R. K. Steunenberg)

a. Dissolution Studies (W. J. Mecham, R. C. Liimatainen, R. Kessie, A. Freeman)

The dissolution step mentioned above has received considerable attention. These data have been reported in ANL-5466, page 13, and ANL-5422, pages 24 to 35. In the latter report kinetic data and the efficiency of hydrogen fluoride utilization were determined under various conditions. It was found that the dissolution rate is increased only to a small extent by an increased hydrogen fluoride sparge rate. The efficiency of hydrofluorination is reduced almost proportionally to the increase in hydrogen fluoride addition rate. A small temperature coefficient corresponding to an activation energy of 6 kcal per mole was found over the temperature range of 600 to 800 C. It was pointed out at the time these data were collected that the rate was very much dependent on such factors as agitation of the melt, vapor-liquid contacting and geometric factors.

(1) Geometry and Pressure Effects

During the past quarter an effort has been made to increase the rate of dissolution by considering different geometrical arrangements and by increasing the pressure in a system of more nearly optimum geometry. Improved contacting during hydrofluorination compared with that in the apparatus described in ANL-5422, page 25 was achieved by using a draft tube to promote circulation. A schematic of this arrangement is shown in Figure 2. The effects of pressure and sparge rate on the dissolution of uranium-zirconium fuel element sections are shown by the penetration rate data given for the runs presented in Table 1. In Figure 3 these data are plotted and show that the penetration rate varies as approximately the 0.9 power of the mass sparge rate. No effect of pressure is evident. Aluminum was included in the materials considered since it is used in enriched reactor fuels.

Additional information on other materials was obtained by using an alundum draft in Run 52c

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Table 1

DISSOLUTION DATA AT 600 C IN NaF-ZrF₄ MEDIUM

The materials dissolved in the above runs had the following form:

- Al: rectangular slice of 2S aluminum, 125 mils thick
- Zr-U: STR assemblies with 3 or 4 plates plus headers, plates and headers 87 mils thick. 1.5 per cent tin, 1 per cent (overall) uranium, remainder zirconium
- Al₂O₃: aluminum crucible wall, 125 mils thick

See Figure 2 for description of equipment.

<u>Run No.</u>	<u>Material Dissolved</u>	<u>Pressure (atm)</u>	<u>HF Rate (grams/min)</u>	<u>Penet. Rate (mm/hr)</u>
D-45-a	Al	1	0.69	0.14
D-45-b	Al	1	0.46	0.02
D-49	Zr-U	1/2	0.25	0.07
D-53	Zr-U	1/2	0.42	0.14
D-48	Zr-U	1	0.70	0.13 ^a
D-52-c	Zr-U	1	0.66	0.18 ^b
D-50	Zr-U	2	0.43	0.14
D-51	Zr-U	2	1.14	0.37
D-52-a	Al ₂ O ₃	1	0	0.05
D-52-b	Al ₂ O ₃	1	0.66	0.06

^a1.0 wt % Al₂O₃ in melt

^bZr-U assembly in Al₂O₃ draft tube

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FIGURE 2.

DISSOLVER - DRAFT TUBE ASSEMBLY.

Melt Volume 107 ml

Reaction vessel has close fitting
liner with flange.

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FIGURE 3.

DISSOLUTION OF Zr-U ASSEMBLIES AT
600 C USING A DRAFT TUBE.

For experimental details see Figure 2 and Table I.

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instead of a nickel tube. Some penetration data were also obtained on alundum itself. It was observed that the rate of attack of the nickel draft tube for both hydrofluorination and fluorination was in the range 0.06 to 0.08 mil/hr. The highest penetration obtained (2 atm Run D-51) corresponds to about a 3.5-hour dissolution for a complete plate 87 mils thick.

(2) Measurement of Dissolution Rate by Hydrogen Metering

During the dissolution of the zirconium-uranium alloy, two moles of hydrogen are produced per mole of metal dissolved. Determining the amount of hydrogen evolved, therefore, provides a means of remotely determining both the rate of dissolution and the completion of the dissolution. The analytical train used in the tests on hydrogen collection is shown in Figure 4. The hydrogen fluoride is collected in cold traps. The hydrogen passes through and is measured by the wet test meter and is reacted with copper oxide in a furnace.

Two blank runs (D-58 and D-59) were made in which hydrogen and hydrogen fluoride were bubbled through the melt to check the efficiency of the collection system. Within the limits of accuracy of the meters (± 5 per cent) the hydrogen input equaled the output.

The results of Run D-60 in which a Zircaloy assembly was partially dissolved are shown in Table 2. A plot of the rate of hydrogen evolution versus time is shown in Figure 5. These data indicate that the method will be useful to follow the dissolution of the STR type fuel elements.

(3) Carry-over of Activity During Dissolution

An active run was made and is reported in detail on pages 28 to 30 of this report. Some data were obtained on the volatilization (or entrainment) of activity during the dissolution step. It was found that 0.2 per cent of the uranium and 0.4 per cent of the niobium were condensed with the excess hydrogen fluoride in the particular equipment used. The amounts carried over for ruthenium, zirconium, and cesium were 0.02, 0.0004 and 0.02 per cents, respectively.

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FIGURE 4.

ANALYTICAL TRAIN FOR DETERMINING HYDROGEN EVOLUTION.

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FIGURE 5.

RATE OF DISSOLUTION OF ZIRCALOY
AS MEASURED BY
HYDROGEN EVOLUTION^a

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Table 2

COMPARISON OF METHODS FOR DETERMINING DEGREE OF DISSOLUTION

Data from Run D-60

See Figure 2 for equipment description

<u>Method of Determining Extent of Dissolution</u>	<u>Indicated Per Cent Dissolved</u>
1. Weight loss of Zircaloy ^a assembly	84 ^b
2. Hydrogen volume by wet test meter	79
3. Hydrogen by weight loss of CuO	65

^aMeat of sandwich 3 per cent uranium, 1.5 per cent tin;
overall composition 1 per cent uranium.

^bBecause it is necessary to scrape off a black film
adhering to the metal there is an uncertainty of
several per cent in this number.

b. Fluorination Studies

(R. Kessie, R. C. Liimatainen, W. J. Mecham,
S. Vogler, K. Schoeneman, A. Freeman)

Data are reported in ANL-5422, pages 31 to 35 and
in ANL-5466, page 15 on the step in which the uranium dissolved in the
fused salt was volatilized by fluorinating to the hexafluoride. In these
experiments it was demonstrated that bromine pentafluoride is an at-
tractive fluorinating agent. Kinetic data were presented indicating that
from the melt analysis 99.5 per cent or more of the uranium could be
volatilized in an hour. This rate is, of course, a function of gas
contacting efficiency, mixing of the fused salt and geometry of reactor.

(1) Comparison of Fluorinating Agents

It was of interest to compare the effectiveness
of various fluorinating agents. Bromine tri-
fluoride is not included since its high boiling
point (125.7 C) makes it more difficult to
volatilize it rapidly through the melt. The
results are summarized in Table 3. It is
indicated that when either bromine pentafluoride,

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TABLE 3

SUMMARY OF DATA FROM URANIUM RECOVERY RUNS AT 600°C

Run No.	Charge		Charge		Sparge Gas	Sparge Rate ^(a)	Time (min)	Pressure (atm)	Amounts Expressed as % of Charge		
	Material	Weight (grams)	Melt ^(c) Gram Moles	UF ₄ Gram Moles					U Recovered Overhead	U Retained in Melt	U Material Balance
D-41 no draft tube	Zircaloy ^(b)	72.920	4.0	0.0031	BrF ₅	1.0 x 10 ⁻³	15	1	-	9.9	-
							30		-	0.7	-
							60		-	0.1	-
							90		129.7	0.4	129.7
D-42 no draft tube	Uranium ^(b)	0.959	2.4	0.0040	F ₂	13.3 x 10 ⁻³	15	1	-	0.03	-
							30		-	0.01	-
							45		-	0.01	-
							60		86.5	0.01	86.5
D-43	Zircaloy ^(b)	57.913	2.6	0.0024	BrF ₅	8.7 x 10 ⁻³	15	1	-	0.11	-
							30		-	0.03	-
							45		-	0.03	-
							60		96.0	0.03	96.0
D-46	UF ₄	1.059	2.6	0.0034	ClF ₃	5.2 x 10 ⁻³	15	1	95.6	0.04	95.6
D-47	UF ₄	0.980	2.6	0.0031	BrF ₅	1.4 x 10 ⁻³	15	1/2	-	52.2	-
							30		-	0.46	-
							45		119.0	0.02	119.0

(a) Sparge Rate = $\frac{\text{moles fluorinating agent}}{\text{hour, ml melt}}$

(b) Metal first dissolved by hydrofluorination.
The overhead line was washed after each run except D-46.

(c) Approximately equimolar in NaF and ZrF₄.

chlorine trifluoride, or elemental fluorine is used as a fluorinating agent, substantially all of the uranium is removed from the melt in less than an hour of sparging. It appears that runs with a higher sparge rate show faster removal of uranium hexafluoride from the melt (Runs 43 vs 47). The runs with higher removal rate also used a draft tube.

(2) Consideration of Material Balance Problems

The material balances for uranium reported in Table 3 are better than those observed in earlier work. However, it was appropriate to see if they could be further improved. The small amounts of uranium handled complicate the problem, but it is important to establish that complete uranium recovery is possible. Four runs were made, the main purpose of which was to demonstrate complete recovery of uranium. Success was limited, with only half the runs yielding acceptable results.

The equipment previously used for the dissolution experiments (ANL-5422, page 24) was modified so that bromine pentafluoride, hydrogen fluoride or fluorine could be sparged through the melt and metered continuously by means of a calibrated thermal flowmeter. The total amount of material used for an experiment was determined from the initial and final weights of a nickel container. The liner tube has now been made with a flange, so that the annulus between liner and furnace tube was sealed off from the reactant gas. The furnace tube contains a thermocouple well, sample port, gas inlet and gas outlet lines. The offgas line has been kept short and leads to the collection vessels, the first of which is a 250-ml nickel vessel with a downleg at -20 to -30 C. The second is a U-tube filled with perforated nickel packing at -60 C. The offgas lines are wound with resistance wire and are kept at approximately 80 C. Approximately 1.5 g of uranium tetrafluoride were added to 209 g of sodium fluoride-zirconium fluoride (1:1 mole ratio) for each run. The temperature was kept at 600 C and helium sparging for one hour was used as a means of stirring, in order to obtain a uniform melt. The bromine pentafluoride sparging was then started and continued for two hours. Samples of the melt before and after bromine pentafluoride sparging and of the bromine pentafluoride in the receiver were analyzed for uranium. Because of the limited accuracy of the method for analyzing uranium

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in the melt, the weighed amount of uranium tetrafluoride was used for all calculations. For analyses of the melt, a 1-gram sample was dissolved in 50 ml of a solution 0.4 M aluminum nitrate and 4 M nitric acid. A portion of this aqueous solution was analyzed by the fluorophotometric uranium method. To analyze the bromine pentafluoride, an approximately 3-gram sample was hydrolyzed in 50 ml of 1.6 M nitric acid. This aqueous solution was then analyzed by the X-ray fluorescence method. The U-trap contents were hydrolyzed by passing warm 1.6 M nitric acid through the cold U-trap. The aqueous solution was analyzed for uranium by the fluorophotometric method. The results are given in Table 4.

The results clearly show that again greater than 99 per cent of the uranium was volatilized from the melt. Collection of uranium hexafluoride was erratic with two of the results being close to acceptable. Attempts to find the missing uranium by washing out the lines with warm nitric acid were unsuccessful. The two runs with high uranium recovery indicate that complete recovery is achievable, probably merely by refinement of the laboratory technique.

The erratic and poor recoveries of bromine pentafluoride also required explanation. The missing bromine pentafluoride could be lost either by escape from the system or by reaction within the system, i.e., the melt or lines. Since each of the previous runs had been made with a fresh melt, attention was focused on the melt as the source for the poor bromine pentafluoride recoveries. A series of runs were made wherein the bromine pentafluoride losses could be compared for a fresh melt and a fluorinated melt.

The results in Table 5 indicate that with a previously fluorinated melt, there is a small loss in passing BrF_5 gas through the zirconium fluoride-sodium fluoride melt. When a new melt is used, there is a much larger loss of bromine pentafluoride.

If the following reaction is assumed

then the unrecovered bromine pentafluoride would represent the presence of 10 mole per cent zirconium oxide. Analysis by I. Sheft of the Chemistry Division of the zirconium tetrafluoride for oxygen

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Table 4

URANIUM RECOVERY FROM MOLTEN ZrF_4 -NaF WITH BrF_5 SPARGING

Melt Composition: 1 mole NaF
 1 mole ZrF_4
 0.0048 mole UF_4
 60 ml melt

Temperature: 600 C

Time: 2 hr

Run No.	FF55	FF56	FF57	FF58
BrF_5 Flow Rate gpm	0.49	0.39	0.37	0.33
Total Material Balance - Per cent ^a				
Receiver	89.2	79.5	83.1	80.0
U Trap	0.6	12	1.5	2.1
Total	89.8	91.5	84.6	82.1
Uranium Material Balance Per cent				
Receiver	81.5	101.3	89.4	94.5
U Trap	0.02	0.7	0.7	0.6
Wash ^b	0.03	0.10	0.6	0.2
Melt	0.8	0.15	0.14	0.3
Total	82.3	102.2	90.8	95.6

^aUranium plus fluorinating agent.

^bAn aqueous wash of the downleg of the first trap.

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Table 5

LOSS OF BROMINE PENTAFLUORIDE IN SPARGING MOLTENZIRCONIUM FLUORIDE-SODIUM FLUORIDE

Melt Composition: 1 mole NaF
 1 mole ZrF_4
 60 ml melt⁴

Temperature: 600 C

Time: 2 hr

<u>Run No.</u>	<u>Time (Hr)</u>	<u>BrF₅ Distilled (g)</u>	<u>BrF₅ Collected (g)</u>	<u>Loss (g)</u>	<u>% Recovery</u>	<u>Remarks</u>
60	2	73.12	65.92	7.30	90.2	New Melt -- Prefluorination of equipment
61	2	136.61	128.48	8.13	94.0	New Melt
62	2	56.06	55.36	0.70	98.8	Fluorinated Melt
63	4.5	177.13	174.92	2.21	98.8	Fluorinated Melt

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content by a fused salt (KBrF_4) modification of the method of Hoekstra and Katz² indicated 2.5 weight per cent oxygen corresponding to 12 mole per cent ZrO_2 . Thus, it appears that the poor bromine pentafluoride recoveries may be explained by the reaction of bromine pentafluoride with zirconium oxide present in the zirconium tetrafluoride.

(3) Fission Product Behavior During Fluorination

It is expected that small amounts of various fission products will be volatilized from the fused salt system during the fluorination step, i.e., ruthenium pentafluoride (bp 313 C) and niobium pentafluoride (bp 233 C). These species will very likely not be collected quantitatively with the uranium hexafluoride but will deposit in the cooler parts of the equipment before the cold traps. The behavior of plutonium is also interesting since it, in theory, might be fluorinated to the hexafluoride. If such is the case the problem of plutonium hexafluoride decontamination is not serious since it can be reduced to the non-volatile tetrafluoride by bromine trifluoride. It is also possible that the hexafluoride will be decomposed to the tetrafluoride in the cooler parts of the equipment. In the shorter-cooled fuels tellurium may also be volatilized.

Fission product volatilization from the melt is not expected to constitute a major problem since it is planned to purify further the uranium hexafluoride by distillation. A satisfactory decontamination of uranium hexafluoride in this manner will not be difficult since the fission product fluorides have boiling points considerably different from that of uranium hexafluoride. However, it is necessary to obtain some data so that the problem of collecting the fission products for waste storage may be evaluated.

In two of the uranium recovery experiments, fission product behavior was observed by adding individual fission product tracer to the melt before treatment

²Hoekstra, H. R., and Katz, J. J., Analytical Chemistry 25, 1608-12, (1953)

with the bromine pentafluoride. Ruthenium was added as the metal and niobium was added as the oxide. After addition of the fission product tracer the molten salt was agitated for one hour by passing helium through the melt. The melt was sampled before and after the two-hour bromine pentafluoride addition. The bromine pentafluoride solution was also sampled. Samples were analyzed for the fission product by counting in the well scintillation counter. The results are given in Table 6.

The results indicate that the volatile fluorides of ruthenium (RuF_5 , bp 313 C) and niobium (NbF_5 , bp 233 C) are removed from the melt to the extent of approximately 90 per cent. The recovery of only approximately 12 per cent of the amount charged strongly indicates that much of the volatile fission product is depositing on the metal walls.

Table 6

BEHAVIOR OF RUTHENIUM AND NIOBIUM DURING THE RECOVERY
OF UF_6 WHEN TREATING ZrF_4 -NaF MELTS WITH BrF_5

Activity level 2×10^7 c/m of ruthenium and 1.2×10^7 c/m of niobium in 60 ml of melt.

	<u>Per Cent Initial Activity</u>	
	<u>Ruthenium</u>	<u>Niobium</u>
In Melt after Fluorination	11.6	12.4
In BrF_5 Solution	0.9	1.5

The next experiment (Run D-44) made used an irradiated portion of an STR fuel element. It had been irradiated for 1560 megawatt days and cooled for 365 days.

The equipment used was the 2-inch dissolver shown in Figure 3, page 18. In this experiment 300 grams of equimolar sodium and zirconium fluorides were

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used. The irradiated material was dissolved by passing hydrogen fluoride through the melt for 6 hours. The melt was then fluorinated with bromine pentafluoride for 45 minutes. The hydrogen fluoride condensate, the contents of the traps, the fused salt residue, and washings of the upper flange and overhead line were all analyzed for uranium, niobium, ruthenium, zirconium, and cesium. The results are reported in Table 7 and indicate the following points.

- (1) A significant amount of activity comes over with the hydrogen fluoride during the dissolution of the STR alloy--most likely by the mechanism of entrainment.
- (2) The amounts of fission products in the overhead with the bromine pentafluoride vary roughly in proportion to their volatility.
- (3) Nickel surfaces in the relatively cooler portion of the equipment serve as an absorber of activity; this would suggest the use of a nickel-packed section to give more area for such decontamination.

There is a difference between the ruthenium results in Tables 6 and 7. In the first experiment 12 per cent of the ruthenium remained in the melt while in run reported in Table 7, 92 per cent remained in the melt. The results for niobium agreed satisfactorily, i.e., 12 per cent compared with 11 per cent. The two experiments differ in the form of ruthenium and niobium used as starting materials and in the fluorination time. Thus, in the first experiment ruthenium metal, niobium pentoxide and a fluorination time of 2 hours were used, while in the second experiment fission product activities and a fluorination time of 45 minutes were used. It is possible that these differences account for the different ruthenium behaviors.

c. Corrosion Investigations
(W. Seefeldt, L. Hays)

Further tests were made to determine the limitations of nickel as a possible material of construction for a fluorination process in fused salt medium. All runs were made at 700 C. The melt was 50 mole per cent sodium fluoride in zirconium tetrafluoride and the sparge was bromine pentafluoride. Variables investigated included the effect of the addition of uranium hexafluoride to the sparge gas, and addition of nickel as nickel fluoride or oxide to the melt. A partial summary of the data appears in Table 8. The temperature selected for the corrosion tests is

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TABLE 7

BEHAVIOR OF URANIUM AND VOLATILE FISSION ACTIVITIES IN ACTIVE RUN

Data from active Run D-44

Conditions of run: 300 grams melt 6-hour hydrofluorination
 600°C temperature 45-minute BrF₅ fluorination
 1 atm pressure

(—————→ decreasing volatility of fluorides —————→)					
Input	U	Nb	Ru	Zr	Cs
A. Charge to Dissolver	0.776 gram	6.32 x 10 ⁹ c/m	0.16 x 10 ⁹ c/m	4.3 x 10 ⁹ c/m	0.64 x 10 ⁹ β c/m
(amounts of output expressed as per cent of charge)					
Output					
B. HF Condensate	0.18	0.35	0.02	0.0004	0.02
C. Overhead					
1. Traps (-20 C, -70 C in Series)	78.0	0.8	0.9	0.02	0.1
2. Washes of Upper Flange and Overhead Line	2.6	45.7	3.6	0.7	0.1
3. Sum of B, C-1 and C-2	80.8	46.9	4.5	0.7	0.2
D. Residue(a)	0.3	10.8	91.9	65.1	112.1
E. Material Balance	81.1	57.7	96.4	65.8	112.3

(a) Defined as the sum of the following: Dissolver sparge line wash, draft tube wash, thermowell wash and melt, and draft tube dissolver.

TABLE 8

RESULTS OF CORROSION STUDIES IN FUSED NaF-ZrF₄ UNDER FLUORINATING CONDITIONS

Material: Nickel
 Fused Salt: Equimolar NaF-ZrF₄
 Sparge Gas: BrF₅
 Temperature: 700°C
 Melt Weights: 300-325 gm

Run	Exposure Time, hr	Additives to		Sparge Rate, g/hr	Dimensional Change, mils/day						
		Sparge Gas	Melt		Avg Impingement Plate Thickness,	Impingement Plate Hole Size			Radial Spoke Diameter		
						max	min	avg	max	min	avg
15	25			12					9	2.8	6.4
16	24			11					11	1	3.8
17	24		Ni powder	9					6.5	0	3.0
18	24		NiO	10					6.6	0	1.9
19	10	10% UF ₆		118					42	18	25
20	24			19	5	11	3.5	7			
21	10			85	19	56	19	34			
22	24		NiO	4	4	5	2.5	3.4			
23	24		NiO	8	6	16	0	6.9			
24	20	10% UF ₆		21	9	23	13	17			
25	20		NiF ₂	6	0	0	0	0			
26	20		NiF ₂	18	8	12	9.6	10			

100 C higher than the expected operating conditions and the lowest sparge rate used was 4 g/(hr) (g melt).

The apparatus used for corrosion testing is shown in Figure 6. Sparging of the melt can be done with helium, bromine pentafluoride, or bromine pentafluoride-uranium hexafluoride mixtures with or without helium dilution. The equipment is readily adapted to operation with other halogen or interhalogen compounds. A safety cut-off on the still pot permits unattended operation. The sparge assemblies are designed for providing impingement corrosion evaluation, that is, the corrosion occurring at points of direct contact with the stream of sparge gas.

Two basic assemblies were used in the series of runs reported. The "radial spoke" assembly shown in Figure 7 consisted of a number of short 1/8-inch OD nickel rods welded radially to a central sparge tube. Each rod was displaced 90° counter-clockwise from the one below. The open end of the sparge tube faced down and was 3/4 inch below the lowest "spoke." The second assembly was the impingement plate. A 1/4-inch thick nickel disc was welded on to the central sparge tube about 3/4 inch above its open end which faced down. Four 1/8-inch holes were drilled in the plate to vent rising gases that might prevent adequate alternate contacting of fused salt and gas.

The following were monitored to determine the corrosiveness of the environment: (1) the vertical and horizontal dimensions of the spokes of the "radial spoke" assembly, (2) the thickness of the impingement plate, (3) the size of the four holes in the impingement plate, (4) wall contours of the nickel container, and (5) the sparge lines.

The data were plotted in Figure 8 and 9 and indicate a possible relationship for flow rate and rate of attack for the several variables. The data for helium-diluted bromine pentafluoride are from ANL-5466. It appears that the least corrosive system for a given flow rate is the sparging of clean melt by helium-diluted bromine pentafluoride; the most corrosive, the sparging of clean melt by bromine pentafluoride to which uranium hexafluoride has been added. Additions of nickel powder, nickel oxide or nickel fluoride to simulate the accumulation of corrosion products in the melt appear to have an accelerating effect, but not a substantial one. Radial spoke data do not confirm this. In Runs 17 and 18 where nickel and nickel oxide additions were made, rates of attack were lower than those in Runs 15 and 16 where no additions were made. Run 19 confirms the increase in rate of attack by either increase in sparge rate or the addition of uranium hexafluoride to the sparge gas or both. The data in Figure 8 and 9 are average penetrations; generally, maximum penetration appears to be about double the average.

Several liners and sparge tubes have been examined to procure additional information. Wall contours of liners have been obtained by microscopically measuring cross sections. In general the contours are similar to those previously reported (ANL-5466, page 22). Attack is consistently most severe near the bottom with a lesser attack occurring

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FIGURE 6.

FUSED FLUORIDE CORROSION TEST APPARATUS.

www Heated Lines

Details of Two
Sparge Assemblies.

FIGURE 7.

CORROSION OF SPARGE TUBE IN RADIAL SPOKE ASSEMBLY.

Melt: Equimolar NaF-ZrF₄

Temperature: 700 C

Sparge Gas: BrF₅

Exposure: 111 hours

Runs: 15 through 19

Numbers shown are reductions in wall thickness.

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FIGURE 8.

RATE OF REDUCTION IN THICKNESS OF IMPINGEMENT PLATES IN FUSED FLUORIDE CORROSION TESTS.

Melt: Equimolar NaF-ZrF₄

Temp: 700 C

Numbers along points indicate run number

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FIGURE 9.

RATE OF INCREASE (AVERAGE) OF HOLE
DIAMETERS IN IMPINGEMENT PLATES
IN FUSED FLUORIDE CORROSION TESTS.

Melt: Equimolar NaF-ZrF₄

Temperature: 700 C

Numbers along points indicate run number

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at the interface. In two liners used in Runs 20 through 24 no interface effects were evident. Penetration did occur unexpectedly in Run 23 at a point midway between the interface and the bottom at an elevation coinciding with the impingement plate. The geometry of the plate and liner wall probably caused sparge gas to channel to the point of failure. Starting with Run 24, a single liner is to be used for each run to eliminate the averaging out of points of maximum attack as they change from run to run. The result from Run 24 indicates the higher maximum attack thus measured. Liner data are shown in Table 9.

Examination of sparge tubes has been made to determine (1) the rate of attack of the tube wall and (2) the shortening of the tube. The data have not been correlated with run conditions. Three sparge assemblies were used (Runs 15 through 19, 20 through 23, and 24 through 26). The wall of each sparge tube had been penetrated at the gas exit during the last run in which each had been used. Assuming that failure occurred in the last hour of the last run penetration rates correspond to 13, 9, and 15 mils per day. Assuming failure in the first hour of the last run, these figures become 16, 13, and 20 mils per day. The rates of shortening of the tubes have been higher. Direct measurement of the tubes indicate average end attack of 65 to 87 mils per day. The sparge tube used in Runs 15 through 19 was sectioned at various elevations and wall thicknesses measured. The results are shown in Figure 7. The corrosion was primarily on the exterior of the tube where alternate sparge gas and melt contacting occurred.

d. Construction and Testing of a Thermal Flowmeter
(W. J. Mechem, R. C. Liimatainen, R. Kessie, A. Freeman)

A thermal flowmeter has been developed which is well suited for metering fluorinating gases at elevated temperatures and over a wide range of flow rates. A sketch of this instrument is shown in Figure 10. The principle of operation is the following. Temperature gradients are established in the tubes connecting the heated block with the cooled block. The flow of gases through the tubes creates a temperature differential in the flowing stream. This differential is measured with a thermopile between the points A and B. A constant temperature difference of 290 C is maintained between the blocks by a temperature controller. Figure 11 shows the calibration of this meter³ with three gases and a comparison with a flowmeter of an earlier design which had a limit of about 500 cc/min in its useful range. From the figure it is clear that the distressing maximum of the Mark 1 model has been eliminated.

³Johnson, K. O., Peed, W. F. and Clewett, G. H. C 5.355.8
June 24, 1946.

Table 9

CORROSIVENESS OF FLUORINATED NaF-ZrF₄ AS MEASURED IN
NICKEL CONTAINERS

Sparge Gas: BrF₅

Temperature: 700 C

<u>Runs</u>	<u>Exposure Time, Hr</u>	<u>Interface Attack^a</u>		<u>Max Attack^b</u>	
		<u>(mils)</u>	<u>(mils/day)</u>	<u>(mils)</u>	<u>(mils/day)</u>
3 through 6 ^c	192	10	1.3	20	2.5
17 through 19	58 plus	9	3	15	4.8
	14 misc				
20 through 23	82	None		35(penetrated)	10
24	20	Evident		11	14

^aDetermined by microscopic measurement of sectioned container.

^bMax attack occurs in bottom 1/2 inch of liner.

^cWall contours of this liner appeared in ANL-5466, page 22.

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FIGURE 10.
THERMAL FLOWMETER.
MARK 2.

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FIGURE II.

CALIBRATION OF THERMAL FLOWMETER.

Potential Generated by Thermopile (Points A and B, Figure 10) vs Flow

e. Other Fluoride Volatilization Approaches to STR Processing
 (R. C. Liimatainen, W. J. Mecham)

An alternative scheme for processing zirconium matrix enriched uranium fuels is to dissolve the alloy in hydrofluoric acid and then remove water, fluorinate and recover the uranium hexafluoride by volatility methods. Such a plant process probably would utilize fluidization for the drying and fluorination steps.

Five fixed-bed fluorinations were carried out to provide initial information on vapor phase fluorination of a solid bed. A summary of the data is shown in Table 10. For Runs D-54 through D-57 the residue was prepared by first treating Zircaloy (1 per cent uranium, 1.5 per cent tin, balance zirconium) with a 2 M hydrofluoric acid solution and then evaporating to dryness. Under these conditions uranium tetrafluoride precipitates as the dissolution proceeds. For Run D-62 a homogeneous solution of the zirconium and uranium fluorides was prepared by dissolution of the alloy with a solution of low fluoride to zirconium ratio. The approach permitted sampling a liquid rather than a solid phase to obtain the uranium content of the reactor charge. The data from some experiments on a dried residue prepared from the aqueous hydrofluoric acid dissolution of an STR fuel element show that the major portion of the uranium can be volatilized. Except for Run D-62 the figures given for material balance are calculated on the basis of estimated uranium content of the fuel material. Therefore, they are probably not particularly reliable. In Runs D-54 through D-57 the uranium left behind is too great for direct process application. The experiments are promising enough to justify further work. In Run D-62 the residue for fluorination was prepared by evaporation to dryness of an initially homogeneous solution, and it appears to be much more difficult to fluorinate the uranium. This residue preparation procedure probably gives a very intimate mixture of zirconium and uranium fluorides. The complete fluorination of the uranium may thus be rendered difficult by coating of uranium fluoride by zirconium fluoride. In all the other experiments the uranium tetrafluoride was precipitated during dissolution of the fuel element sample due to the higher fluoride concentration.

2. Processing of Uranium-Plutonium Alloy Systems
 (R. C. Vogel, M. Steindler, F. Linzer)

The possibility of adapting a complete fluoride volatilization scheme to plutonium-containing fuels is being approached by investigating the preparation and properties of plutonium hexafluoride. The dissolution of uranium-plutonium alloys (i.e., Hanford fuel elements) in bromine trifluoride forms uranium hexafluoride but fails to volatilize plutonium, leaving it behind as an insoluble residue. It is believed possible to devise an all-volatility separations scheme for uranium-plutonium alloy systems by a high temperature (400 to 600 C) gas-phase fluorination of this residue. The current experimental effort is directed toward an investigation of the optimum conditions for plutonium hexafluoride preparation and a study of the best methods of handling the compound. The approach to the problem has been outlined earlier (ANL-5422, page 35).

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TABLE 10

URANIUM RECOVERY FROM VAPOR-PHASE BrF_5 FLUORINATION OF A FIXED SOLID BED

Experimental details: 1. U-Zr-Sn(a) alloy dissolved in aqueous HF solution.
2. Liquid evaporated.
3. Residue charged to vertical, nickel reactor
(3/4" diam x 7" long) for fluorination.

Residue for runs D-54 through 57 prepared by evaporating solution initially containing UF_4 precipitate.

Residue for run D-62 prepared by evaporating homogeneous solution.

Run No.	Material in Bed ^(a)		Time of Fluorination (Minutes)	Amounts Expressed as Per Cent of Charge		
	Average Temp C	Size		U Recovered Overhead	U Left in Reactor	U Material Balance
D-54 1	400(a)	20-40 mesh	60	108	-	-
2			60	1.9	18	128(d)
D-55 1	400(b)	60-200 mesh	45	128	-	-
2			45	4.3	12	144(d)
D-56	475(b)	40-80 mesh	45	69	1.5	70(d)
D-57	600(c)	20-40 mesh	135	50	4	54(d)
D-62	600	20-200 mesh	105	28	65	93

(a) Original alloy contained 95.3 per cent zirconium, 3.7 per cent uranium and 1.0 per cent tin.

(b) Upon introduction of the BrF_5 the temperature of the bed rose about 15 C because of reaction with water which was not removed in the drying steps.

(c) ~35 C temperature rise upon fluorination because of no helium drying at 300 C; the temperature was gradually raised to 600 C during the first hour of operation.

(d) These material balance figures are based on an estimated fuel element uranium content.

Apparatus for these studies has been completed and a small amount of plutonium hexafluoride has been prepared. The experiments will be described in greater detail when more data are available.

3. The Formation of Bromine Monofluoride
(R. K. Steunenber, R. C. Vogel, G. Redding)

In the dissolution of uranium which presumably takes place according to the reaction

anomalously high pressures were often measured in the closed vapor space above the liquid. It was thought that these pressure increases were probably due to the formation of bromine monofluoride, a compound which is not well characterized. It has, therefore, been of interest to investigate the reaction

It has been established that this reaction does occur in the vapor phase and that it is very likely the only chemical reaction occurring. This reaction can account for the increases in pressure observed during the dissolution of uranium. The equilibrium constant has been measured at 75 C.

Data are reported in ANL-5422, page 44 to 47 and ANL-5254, page 43 to 48, on the absorption spectra of bromine and bromine trifluoride. When various amounts of bromine and bromine trifluoride are mixed in the absorption cell it is possible from the absorption spectra and pressure-volume-temperature measurements to calculate the equilibrium constant. The value of K_p obtained from 38 runs under various conditions at 75 C is about 200 cm. A complete statistical analysis of the data is not yet complete. Runs at different temperatures will next be made in order to obtain ΔH for the reaction. The data will be completely reported at a later time in the open literature.

B. Semi-Works Operation
(W. Mechem, R. C. Liimatainen, R. Kessie, O. J. DuTemple)

Construction and procurement of equipment has proceeded for the semi-works scale recovery of decontaminated uranium from STR-type fuel elements by a fluoride volatility process. The major process vessel is a molten fluoride dissolver and sparge unit which will be integrated into the distillation columns of the existing fluoride volatility process pilot plant. The installation is expected to be complete this year.

Also scheduled for the coming quarter are process runs of the existing pilot plant equipment. After shakedown operations, active uranium will be dissolved in liquid bromine trifluoride and recovery of decontaminated

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uranium hexafluoride will be made by fractional distillation. The equipment and basic process flowsheets have been outlined in numerous quarterly reports of this Division.

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IV. CHEMICAL METALLURGICAL SEPARATIONS PROCESS

Details of performance testing of a new shielded furnace are discussed. Investigations of possible liquid oxides for uranium slagging were continued. A differential thermal analysis apparatus for phase diagram investigations in this field was put in operation. The kinetics of boriding tantalum were investigated. Further evidence of the comparative resistance of tantalum boride to uranium attack is given. Five experiments on plutonium extraction from molten uranium by magnesium were carried out. These gave a mole fraction distribution coefficient of 0.07 ± 0.01 (preliminary value). Uranium powders have been successfully formed and dispersed in and filtered from molten magnesium.

In the semi-works, oxidative slagging runs were conducted with fissium, an inactive stand-in for highly irradiated fuel material (2 per cent burn-up of total atoms) prepared by dispersing fission products in uranium by powder metallurgy. Analytical results have been obtained to date on only cerium and cesium decontamination. As in tracer fission product level studies, these were removed essentially completely by the oxidative slagging process. On a 2-kg scale, purified ingot yields from fissium have been around 93 per cent. With fissium, a fairly bulky and porous slag is formed.

Work continued on the testing of various top and bottom pouring techniques.

In work related to magnesium extraction of plutonium, the study of magnesium distillation on a 4-kg scale was begun, various extraction devices are being designed for possible testing, and testing of various materials of construction continued.

A. Laboratory Studies (H. M. Feder)

1. Slagging Investigation (N. Chellew, C. Cushing, D. Finucane, J. Schilb)

Effort during this quarter continued to be directed toward the completion of the shielded, vacuum-casting furnace installation. A preliminary description of this furnace appeared in ANL-5466, pages 32 to 39. The results of the testing procedures carried out are given below.

a. Vacuum System

The furnace chamber has a volume of 160 liters and contains 27 neoprene "O" ring seals. A helium leak detector, stated to have a lower sensitivity limit of 10^{-9} cc/sec, was used for leak hunting. The maximum leak rate at the "O" ring seals was 3×10^{-8} cc/sec of helium. The pressure rise in the blanked off furnace chamber (unheated) was nearly linear at a rate of 16 microns per hour. This corresponds to

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43 micron-liters per minute or 3.1 cc (STP) per hour. Lower leak rates are expected when the furnace walls become more thoroughly out-gassed with usage. In a preliminary experiment with a charge of metal heated to 1320 C a maximum pressure of 0.8 micron was recorded.

b. Resistance Heater Assembly

Several faults in the molybdenum rod heater assembly as received were noted and corrective measures were applied, as follows. Expansion and warpage of the molybdenum heat shields due to heating established contacts with the heater elements which caused shorting of the heater current. Supplementary alumina spacers between shields and heater eliminated this difficulty. The surfaces of all molybdenum parts should be clean and bright before commencing vacuum heating, otherwise the insulators eventually fail to function. The conductivity of the spacers, which become blackened before failure, may be ascribed to deposition and decomposition of sublimed molybdenum trioxide.

The heater assembly platforms, as supplied, were porous, and somewhat fragile, inch-thick slabs of alumina. Cracks appeared in these after one or two heating cycles. A new platform of graphite (for strength), covered with a thin high-fired alumina spacer (for insulation), was fabricated and has been used very satisfactorily.

A cross-section of the heater assembly as it now appears is shown in Figure 12.

c. Resistance Heater Performance

The resistance heater, a coil of 5-mm diameter molybdenum rod with a total length of 210 cm, should come to a reproducible equilibrium temperature depending on power input only, provided that the geometry of the system of heater and shields remains unchanged. In Table 11 the relationship of heater temperature to power input, as determined in four separate sets of experiments, is given. For a given powerstat setting the maximum deviation of power input from the average was 2.7 per cent, and the maximum deviation of the temperature from the average was 3.3 per cent. The average deviations are less than one per cent.

In the temperature range under consideration the equilibrium temperature is determined almost exclusively by radiation losses; an approximately linear relation between the power input and the fourth power of the absolute temperature is to be expected. The data of Table 11 are plotted in this form in Figure 13. The linear relation is very well satisfied and permits a selected heater temperature to be preset readily.

Considerable temperature lags between the heater and the contents of the crucible have been noted. In order to minimize this effect the mass of the graphite crucible holder has been decreased by drilling a number of holes in its side and thinner walled crucibles have been substituted for the thick walled (3/16 in.) thoria crucibles originally used. At the same time the graphite crucible holder has been drilled and tapped to receive some graphite screws. This will permit a variety of crucibles of differing diameters to be held snugly in the holder.

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FIGURE 12.
RESISTANCE HEATING ASSEMBLY.

Table 11

DEPENDENCE OF HEATER TEMPERATURE ON POWER INPUT

<u>Powerstat Setting, Per Cent</u>	<u>Average Power Input, KVA^a</u>	<u>Average Heater Temperature^b, C</u>	
		<u>Corrected for Window Absorption</u>	<u>Corrected for Emissivity of Mo^c</u>
50	2.67	1253	1361
60	3.57	1362	1476
70	4.64	1475	1617
80	5.82	1559	1716
90	7.17	1653	1827

^aProduct of voltage and current input to transformer, with no correction for transformer losses.

^bOptical pyrometer readings made after stabilization of voltage and current, 8 to 20 minutes after each setting.

^cAssumed spectral emissivity, 0.382.

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FIGURE 13.

MOLYBDENUM ROD HEATER
TEMPERATURE vs POWER INPUT.

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d. Mold Design

Three designs of molds for chill casting uranium have been tested for performance. The molds fit snugly into the movable water-cooled mold holders provided with the furnace. The most satisfactory design to date is a copper mold with a 1/4-in. wall thickness and a 2° internal taper. The capacity of the mold is 100 cc. In order to prevent possible spills during top-pouring operations, a funnel of tantalum sheet has been used to guide the flow into the mold opening. A simple mold dressing of graphite dust has been found adequate to prevent the ingot from sticking to the mold. A cast uranium ingot slips out readily from this mold on inversion and leaves a clean interior for the next use. It has also been found expedient to allow the mold to be radiantly heated during the melting operation and to commence water cooling just before the pour. This provides a measure of outgassing of the mold surface and yields an ingot free of surface defects.

After the modifications noted above had been made, an experimental vacuum melt of 932 grams of uranium was made in a magnesia crucible. The charge was top-poured at a temperature 1320 C in one continuous motion. The recovered ingot was 96.8 per cent of the charged metal. It was free of surface defects, blow holes, and pipe. Sections of this ingot have been submitted for a general metallographic study of quality.

e. Inert Gas Purification System

The system which has been installed for inert gas purification is shown schematically in Figure 14. The primary system components are a cooled activated charcoal trap, a molten barium-magnesium bubbler, flow meters, and a dew point indicator modified to permit continuous estimation of water and oxygen content (ANL-5466, page 40). The complex valving arrangement allows changes in the flow sequence to be made readily. When not in operation the system can be pumped down with a small mechanical pump.

The activated charcoal trap contains 200 grams of material. The entering gas is precooled in a spiral copper tube. At a throughput of 5 liters/min of gas the linear flow rate through the bed is 260 cm/min. This choice of operating conditions was influenced by tests made on a one-fourth scale model. The test results are shown in Table 12. It is apparent that under the experimental conditions no breakthrough of water vapor occurs at lineal flow rates below 700 cm/min. It was also demonstrated that at 352 cm/min flow rate the capacity of this system exceeds the 160 liters of gas required to fill the furnace. The capacity is at least 16 liters per gram of charcoal. Removal of about 50 per cent of the oxygen (and, presumably, a fraction of the nitrogen) in this step will place a lighter burden on the succeeding purification steps.

The barium-magnesium bubbler has been charged with 400 grams of metal (9 weight per cent magnesium). A eutectic melting temperature of 358 C has been reported for this alloy⁴. The charge is held in a mild

⁴Klemm, W. and Dinkelacker, F., Z anorg. chem., **255**, 2-12 (1947).

FIGURE 14.
INERT GAS PURIFICATION SYSTEM.

Table 12

PURIFICATION OF HELIUM BY ACTIVATED CHARCOAL

Material: Columbia Activated Carbon, grade AC, 6/14 mesh, 47 gm
 Bed: Diameter 3.3 cm, Height 14 cm
 Coolant: Liquid nitrogen
 Helium
 Pressure: Atmospheric

<u>Linear Flow Rate,</u> <u>cm/min</u>	<u>Feed</u>		<u>Product</u>	
	<u>Water, ppm^a</u>	<u>Oxygen, ppm</u>	<u>Water, ppm^a</u>	<u>Oxygen, ppm</u>
88	6	38	0	21
176	"	"	1	20
352	"	"	0	20
690	"	"	1	-
880	"	"	4	-
1130	"	"	6	-
1340	"	"	12	-
352	4	32	0	17
352	"	"	0	16

^aAfter correction for an instrumental blank of 5 ppm.

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steel crucible inside a heated stainless steel pot. Room temperature tests on a scale model using a liquid of approximately the same density-viscosity characteristics showed that up to 3 liters/min of gas could be bubbled through without splashing provided a number of mild steel Raschig rings (1/4 in. x 1/4 in. x 1/32 in. wall) were inserted to break up large bubbles.

2. Liquid Oxide Slags (M. Ader, J. Bingle)

The system, barium oxide-zirconium oxide, previously discussed in connection with slagging (ANL-5466, page 42), was further investigated. A series of mixtures of zirconia with either barium carbonate or barium oxide was heated under varying conditions of time, temperature, and atmosphere in platinum or alumina crucibles. The latter were perceptibly attacked. In the experiments with mixed powders, evidence for fusion of the desired eutectic after heating to 1450 C was either negative or rendered uncertain by the possibility that liquid was actually formed during decomposition of the carbonate. The eutectic in the system barium oxide-barium carbonate occurs at 1030 C and 33 per cent barium carbonate.⁵ However, after pelleting a charge of barium carbonate and 7.2 wt per cent zirconium oxide under a pressure of 20,000 psi, definite fusion occurred on heating to 1500 C in a platinum crucible open to the air. The weight loss due to evolution of carbon dioxide was 82 per cent of theoretical. Apparently, the intimate contact of particles, which is achieved by pressing the powders, is necessary to speed the interdiffusion required to get the liquid phase.

The differential thermal analysis apparatus for phase diagram studies has been constructed and put into operation. Heat is supplied by a Globar furnace. The furnace tube is refractory porcelain. The furnace cap is water cooled and is provided with the usual accessories for viewing, gas handling, and thermocouple connections. The heart of the equipment is a cylindrical zirconia block drilled to receive two small crucibles (platinum or graphite) having re-entrant wells. Thermocouples (platinum-90 platinum, 10 rhodium) fit snugly into these wells. The block is supported in the hot zone of the furnace by a tantalum bail and rod. A single-pen, zero-centered, 2.5 mv span potentiometer is used to record temperature differences. A multirange instrument is used to record reference temperatures.

The equipment was tested with potassium nitrate and sodium chloride as test substances and calcined alumina as the reference substance. Good agreement with literature values for transition and fusion temperatures was obtained. In the temperature range of 1200 to 1500 C, however, AC pickup caused considerable instability in the thermocouple circuits and resulted in uncertain thermal indications. This difficulty has been nearly entirely eliminated by grounding the thermocouple leads through

⁵Lander, J. J., J Chem Soc, 73, 5893 (1951)

8 microfarad condensers and by installing a grounded Faraday cage around the zirconia block. A test run of pure calcium fluoride gave good indication of freezing at 1414 C, in accord with literature values which average 1416 ± 5 C.

The oxide mixtures to be studied will be pelleted, fused, ground and analyzed before differential thermal analysis curves are taken in order to obviate difficulties of slow and incomplete reactions.

3. Dissolution Studies (M. Beederman)

a. Analytical Dissolutions

Studies of the dissolution of "fissium" alloys for analytical purposes were continued. Even under the most vigorous conditions employed, i.e., boiling aqua regia-hydrofluoric acid mixtures, residues of about 0.1 per cent by weight of the starting alloys remained undissolved. The residues contained principally ruthenium and rhodium and a trace of niobium. To put this material into solution a sequence of steps involving treatments with alkaline hypochlorite--to dissolve ruthenium--and a pyrosulfate fusion may be used. A single fusion with sodium hydroxide-sodium nitrate may be used instead, although the recovery of rhodium is not quite quantitative. Results of analyses of a "fissium" alloy⁶ are reported on pages 69 and 70.

b. Chlorination Reactions

As previously reported (ANL-5466, page 45) a brief study was made of the possibilities of analytical dissolutions of "fissium" alloy by means of a series of fusions to give water soluble products. No advantage over the more conventional techniques was obtained. In the course of this study analogues of the Gibson reaction⁷

with zinc or cadmium chlorides were demonstrated. Similar smooth and quantitative reactions can undoubtedly be carried out with bismuth and stannous chlorides. In the work of Gibson it was shown that partial decontamination of uranium from the metals more noble than lead, i.e.,

⁶Prepared by powder metallurgy by the Sylvania Electric Products, Co., New York

⁷Gibson, A. R. et al, AERE-C/R-1279

molybdenum, ruthenium, and niobium, was achieved. The substitution of other chlorinating agents for lead chloride may be expected to change the distribution of the fission elements because of the change in chlorination potential and because of alloy formation. The appropriate measurements can be carried out very readily with "fissium" alloy.

4. Container Material Studies
(C. Rosen, R. Sweezer)

a. Purity of Amorphous Boron

Many of the difficulties in obtaining reproducible results in boriding experiments have been traced to the unsatisfactory quality of amorphous boron powders, as received. These powders, purchased from two commercial sources, and stated to be 99 per cent pure, were analyzed for boron content by the method of Blumenthal.⁸ The two samples analyzed 94.0 and 94.7 per cent with an estimated accuracy of one per cent. Condensable vapors are released on heating these powders in vacuum above 900 C. Vacuum heating above 1600 C for one-half hour increased the boron content of the residue to 97.0 per cent. The changes in weight of a charge of boron powder heated in a Knudsen oven are shown graphically in Figure 15. Large weight losses which take place soon after the start of heating far exceed those expected from the known vapor pressure of boron.⁹ This behavior, also observed by others, has been ascribed to evaporation of the readily volatile molecule, BO^9 , formed by the reaction of boron and boric oxide,

Vaporization experiments will have to be carried out for longer periods of time in the higher temperature ranges to determine whether or not the rate of weight loss finally approaches that expected from the vapor pressure of boron.

b. Kinetics of Pack Diffusion of Boron into Tantalum

In order to determine the optimum conditions for pack diffusion of boron into tantalum sheet, standardized coupons of 1.4 sq cm area were treated in duplicate at various temperature for 5 minutes. The boron powder was first outgassed at 1000 C. The average weight gains found were (in mg): 1585 C, 21.7; 1830 C, 35.7; 1950 C, 40.0. These values established the order of magnitude of the activation energy for the process at about 13 to 16 kcal (Figure 16). This low value for

⁸Blumenthal, H., Anal Chem, 23, 992 (1951)

⁹Searcy, A. W., and Myers, C. E., unpublished work

FIGURE 15.
LOSS IN WEIGHT OF
AMORPHOUS BORON IN VACUO.

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FIGURE 16.
PACK BORIDING OF
TANTALUM SHEET.
BORON PICKUP vs
RECIPROCAL TEMPERATURE.

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activation energy is evidence that vaporization of boron or boric oxide is not a necessary step in the process and indicates probable diffusion control.

Examination of the surface coatings formed showed that in every case material in the composition range of TaB_2 was formed. At the highest temperatures some contamination with TaC was noted. Reheat of these coatings in vacuum at 1650 C produced only partial reaction to form a mixture of $TaB_{1.8}$ and Ta_3B_4 .

c. Resistance of Tantalum Boride to Uranium

The corrosion resistance of borided tantalum is indicated by a comparison of the effects of molten uranium held at 1350 C for eight hours in an uncoated tantalum crucible (Figure 17a) and in a borided tantalum crucible (Figure 17b). The photomicrographs show clearly that the boride layer has prevented massive attack on the tantalum. The distinct difference in wetting is also evident.

An effort to locate the phase boundaries in the ternary system U-Ta-B by heating and quenching various mixtures gave inconclusive results due to the slow reactions of tantalum in the form of chips. These experiments will be repeated with pressed, mixed powders.

Although it has been reported that powdered TaB_2 is rapidly converted to TaB by heating in vacuum above 1600 C, treatment of a hot pressed TaB_2 crucible at 2000 C for extended periods of time failed to reduce the boron content of the surface below the phase boundary composition $TaB_{1.78}$.

5. Plutonium Extraction with Magnesium (E. Greenberg, M. Nathans, K. Anderson)

Seven plutonium extraction experiments have been made for the purpose of learning operational techniques and sampling methods. The equipment and experimental method have been described in ANL-5466, page 46, and ANL-5422, page 72. The results and pertinent data are given in Table 13. In these experiments the magnesium in the quenched ingot was sampled by cutting slices which were dissolved in dilute sulfuric acid. Dilute sulfuric acid was also used to clean the uranium portion of the ingot from adhering magnesium. The uranium ingots were sampled at various locations by electrolytic drilling with dilute nitric acid. The plutonium concentrations given in Table 13 are each averages of from two to five samples analyzed.

The following comments on these experiments are pertinent:

Runs 1 through 3. Plutonium was introduced in the form of turnings of one per cent alloy. From the appearance of the quenched ingot it was evident that many of the turnings had retained their identity and had failed to mix with the bulk

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Figure 17 - Corrosion of Tantalum by Uranium

Figure 17a

Section Through Uranium Ingot in Tantalum Crucible

10 X

Micro 17885

Figure 17b

Section Through Uranium Ingot in Borided Tantalum Crucible

10 X

Micro 17884

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TABLE 13

DESCRIPTION AND RESULTS OF PLUTONIUM EXTRACTION EXPERIMENTS

Equipment described in ANL-5422, page 72.

Run No.	Heavy Metal Composition	Purity of Magnesium ^a	Crucible Material	Weight of Heavy Metal (gm)	Starting Concentration of Pu in Heavy Metal		Temp-erature (C)	Time at Temp (hr)	Final Pu Concentrations			Material Bal for Pu (%)
					Wt of Mg	Heavy Metal (wt %)			in U (wt %)	in Mg (wt %)	K ^b	
1	Uranium	Commercially Pure	Morganite Alumina	106.48	0.0148	40.04	1161	2	0.0086	0.0057	0.07	~75
2	Uranium	Commercially Pure	Morganite Alumina	115.46	0.0144	45.21	~1160	~1 ^c	0.0090	0.0054	0.06	~75
3	U-5.2% Cr	Commercially Pure	Morganite Alumina	105.32	0.0189	31.47	942	5	0.011	0.0076	0.07	~70
4	Uranium	Commercially Pure	Morganite Alumina	101.04	0.0400	45.33	1181	2-1/2	0.031	0.021	0.07	100
5	Uranium	Commercially Pure	Tantalum	107.56	0.0405	47.02	1173	3	0.029	0.023	0.08	98
6	Uranium	Sublimed	Tantalum	108.17	0.0662	19.23	1174	1-1/4	0.056	0.018	0.03	89
7	U-5.2% Cr	Sublimed	Morganite Alumina	104.76	0.0367	19.77	1171	1-1/4	--d	--d	--d	--d

^aTotal known impurities - commercially pure, 0.013%; sublimed, 0.005%.

$$K = \frac{\text{Mole fraction of Pu in Mg}}{\text{Mole fraction of Pu in U}}$$

^cFurnace winding failed during run; sample not quenched.^dAnalytical results scattered and inconclusive.

phases. The low material balances in these runs is attributed to mechanical sloughing off of these chips during sampling operations. Minor amounts of plutonium, 3 to 6 per cent of the total, were recovered by leaching the crucible and its cover.

Runs 4 through 7. In these experiments plutonium was introduced in the form of pellets of 5 per cent alloy weighing about one gram. No evidences of incomplete mixing were seen in the quenched ingots. Care was taken to dissolve all residues from sampling in aqua regia. The material balances for plutonium in these runs was much improved.

Runs 3 and 7. Sampling uranium-chromium alloys by electrolytic drilling with dilute nitric acid is not feasible. In Run 3 the alloy was sampled by a two-step partial dissolution with 6 N hydrochloric acid and concentrated nitric acid. In Run 7 electrolytic drilling with sulfuric-hydrofluoric acid mixtures was attempted but the results were scattered and inconclusive.

Conclusions from these experiments must be only tentative, pending studies to determine the attainment of equilibrium. Plutonium concentration, container material, temperature and time at temperature were all widely varied. All the distribution coefficients except one fall in the range 0.07 ± 0.01 . In the exceptional case (Run 6), however, not only was the purity of the magnesium used changed but also the weight ratio of the phases; hence, no explanation of the low value of the distribution coefficient, namely, 0.03, is offered.

6. Solid State Diffusion Studies (R. L. Nuttall, J. Settle)

Experimental work on this problem was resumed after a delay caused by occupancy of new laboratory space. Uranium powder, prepared in situ by hydriding and dehydriding a uranium-magnesium mixture, has been successfully suspended in molten magnesium by mechanical agitation. Studies of the dispersion and homogeneity of this material are underway. Good phase separation of suspended solids from molten magnesium has been achieved by filtration through porous graphite.

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

1. Study of Oxidative Slagging on Kilogram Scale (G. Bennett, D. Busch, J. Jones)

In the past quarter a series of 2-kg runs was made (equipment and operating procedure given in ANL-5422, page 75) using fission, which is an inactive, synthetically prepared stand-in for highly irradiated fuel material. Specifically, it is uranium in which fission products have been dispersed by powder metallurgy techniques in concentrations equivalent to about 2 per cent burn-up of total fuel atoms (see page 67). Most of the runs were made at a fission product concentration level

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equivalent to 1 per cent burn-up of fuel. Little analytical information is available since analytical methods for this complex material have not been perfected. However, as in previous slagging work, cesium and cerium were apparently well removed by the slagging operation. Their concentrations in the purified ingot were less than 0.02 wt per cent, as compared with nominal initial concentrations of about 0.15 wt per cent for cerium and 0.11 wt per cent for cesium.

Yields of metal as purified ingot ranged between 90 and 94.4 per cent. On the average, these are very slightly lower than yields experienced with natural uranium, which were about 94 per cent. The slag remaining behind in the crucible is considerably more voluminous than that found with natural uranium. From a 2-kg melt the slag layer was about 1/2 in. thick, the diameter being about 2 1/2 inches. The slag was tough, brittle, and porous, somewhat resembling petroleum coke in appearance.

In general, it was found that fissium behaves similarly to natural uranium. However, the deposits of volatile constituents (mainly cesium) on cold surfaces are very pyrophoric. In order to handle this material safely, a bleeder arrangement was installed which allows a manually varied mixture of air and helium to be passed through the vacuum furnace, thus allowing its contents to be subjected to slow, controlled oxidation. This has worked satisfactorily.

The purified ingot yields and conditions employed in the fissium runs are shown in Table 14.

In all of the above runs the crucibles and accessory equipment were first degassed to a pressure of $\sim 5 \times 10^{-4}$ mm at 1000 C. After charging, with the exception of Run S-5, the crucibles were then degassed to the above pressure at 600 C, then placed under flowing helium at 1 to 2 inches of water pressure. In Run S-5, helium was used throughout the heating cycle.

In each of the above runs, considerable emphasis was placed on attempting to improve the ingot yields by pouring at a temperature of 1400 C, 200 C above the liquation temperature. However, it was found impossible to raise the melt temperature immediately (within 5 to 10 min) from the liquation temperature to the desired pour temperature, and, as longer times were devoted to this final operation, an uncertainty was introduced into both the liquation time and temperature. It was finally concluded that temperature measurements made by optical pyrometers were inaccurate because of the presence of fumes within the furnace unit. Therefore, an immersion thermocouple has been installed (a platinum, platinum-10 per cent rhodium thermocouple in an alundum protection tube) for determining the temperature of the melt. This method of temperature measurement has proved very satisfactory.

Additional slagging runs using fissium are now being made. The variables in these runs will be time of liquation, temperature of

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Table 14

CONDITIONS OF FISSION RUNS

(See ANL-5422, page 75, for equipment and procedure descriptions)

<u>Run</u>	<u>Equivalent Burn-up (%)</u>	<u>Liquation Time (hr)^a</u>	<u>Liquation Temp (C)</u>	<u>Apparent Pour Temp^b (C)</u>	<u>Per Cent Yield</u>
S-1	1	4	1160	1160	90.2
S-2	1	4	1200	No Pour	--
S-3	1	4 + 31 min	1200	1260	94.4
S-4	1	2 + 31 min	1200	1265	93.9
S-5	2	2 + 30 min	1200	1270	91.1
S-6	1	2 + 40 min	1200	Very High >1400 ^b	91.1
S-7	1	4 + 10 min	1200	~1400 ^b or >	--
S-8	1	2 + 54 min	1200	~1400 ^b	93.4

^aMinutes in time column represent time used in heating up to the pour temperature.

^bBy Leeds and Northrup optical pyrometer, except in Runs 6, 7, and 8 in which a temperature of 1400 C or greater was apparently reached.

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liquation, and fission product concentration, i.e., per cent burn-up of fuel. The use of a high pour temperature to improve ingot yield has been discontinued, since high pour temperatures will be realized in the sequence of runs in which the liquation temperature is varied.

In the previous quarterly (ANL-5466, page 52) a brief description was given of two runs made to determine the effect of crucible re-use, with no intermediate slag removal, on fission product decontamination and product yield. In these runs, the uranium alloy charge contained synthetically added cerium and zirconium in concentrations corresponding to 0.1 and 1 per cent burn-up of fuel atoms, respectively. Through this crucible re-use, product yields increased from 92.1 per cent in the initial use to 98.5 per cent on the second use. Decontamination from cerium was essentially unaffected, the purified ingots each containing about 10 per cent of the amount initially present. However, the retention of zirconium increased from 30 per cent to 120 per cent, indicating some zirconium pickup in the second use. Graphite has been shown to be an effective zirconium scavenging agent (ANL-5290, page 93), and could be used to provide good removal of zirconium. However, with the more voluminous slag encountered with fission, it remains to be shown that crucible re-use is practical.

2. Sensitivity of the Ingot Quality and Yield to Some Operating Variables (A. A. Chilenskas, K. Olsen)

The objective of this work is to evaluate, from an operational point of view, the effect of certain variables on ingot quality and yield in the slagging process as presently conceived. The variables to be studied are atmosphere purity, degassing technique, and ingot casting methods.

At present, a vacuum remelt by the metallurgists of the oxide-slugged ingot is planned. However, it is deemed desirable to keep the ingot surface oxidation and slag inclusion to a minimum. Hence, ingot quality will be evaluated with this as a primary consideration. General interest in the microstructure of the ingot exists and this will be evaluated by microscopic and photomicrographic techniques.

While it is recognized that the variables being investigated are probably not the controlling factors in metal recovery from the oxide slagging process, recovery data will be kept to determine whether any of the variables studied have an effect. This will be of special interest during the study of atmosphere purity.

In the past quarter, two different degassing procedures were investigated in two, 2-kg runs made with natural uranium. The first was a natural uranium melt under flowing helium with no prior degassing of the crucible but with a vacuum degassing step performed in sequence with the melting step. The second was a thermal degassing experiment in which the crucible (not charged) was degassed in a separate step by heating to 1200 C in flowing helium.

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In the first experiment, the uranium and system components (crucible, mold, etc) were degassed under vacuum, about 3×10^{-4} mm of mercury, as the temperature was increased to 600 C. Further heating, melting and casting operations were conducted under a flowing stream of purified helium (1 liter/min). After being held molten for fifteen minutes, the metal was cast by bottom pouring into a graphite mold and cooled under helium.

In the second experiment, the system components minus the uranium charge were first heated to 1200 C under flowing, purified helium (1 liter/min). After cooling under helium, the uranium was charged, and subsequently melted and poured into a graphite mold under the flowing inert gas.

Recovery of metal as poured ingot was the same in both runs--98 per cent. With thermal degassing, the cast ingot was smooth and shiny, and its appearance was, in fact, superior to the ingot obtained in the first run which involved some vacuum degassing. Some areas on the top and sides of the ingot from the run in which vacuum degassing was employed were coated with a black skin. Thus, thermal degassing seems a satisfactory method for producing good quality ingots.

3. Fissium

In the last quarter, 350 of the 1000 pounds of "fissium" being supplied by Sylvania Electric Products, Inc were received. This is uranium in which most of the fission products as powders are incorporated into uranium metal by powder metallurgy techniques. Fission product concentrations are equivalent to a 2 per cent burn-up of total fuel atoms. This material is being used in experimental work as a stand-in for the discharged fuel from the EBR-II reactor.

Table 15 gives the nominal composition of the fissium and the form in which the fission products were added. The powders were mixed under an inert gas atmosphere and compacted into cylinders 1 3/8 inches in diameter by 4 5/8 inches in length at a temperature of 600 C and a pressure of 12 tons/sq in.

Development of chemical analyses for the major fission product elements in fissium is underway, but there are no analyses to report at this time. Considerable difficulty has been encountered in dissolution of the fissium. It is possible, however, to dissolve it using successively, aqua regia containing fluoride ion, treatment of the residue with hot sodium hypochlorite, and a fusion of any remaining residue with potassium pyrosulfate, the fusion mass being dissolved in sulfuric acid. Other dissolving procedures are also being investigated.

Metal samples of Sylvania fissium, piece AF-7, end and center, were submitted to the spectroscopy laboratory for analysis. The metal was converted to the oxide prior to analysis. Some material, e. g., antimony, may have been lost in this operation.

Table 15

NOMINAL COMPOSITION OF FISSIUM^a

<u>Element</u>	<u>How Added</u>	<u>Nominal Conc (wt per cent)</u>
Strontium	as hydride ^b	0.04
Zirconium	200 mesh powder or as hydride ^b	0.18
Niobium	200 mesh powder	0.01
Molybdenum	325 mesh powder	0.16
Ruthenium	200 mesh powder	0.25
Rhodium	200 mesh powder	0.04
Palladium	200 mesh powder	0.14
Silver	300 mesh powder	0.02
Cadmium	325 mesh powder	0.01
Tin	325 mesh powder	0.003
Antimony	325 mesh powder	0.004
Tellurium	200 mesh powder	0.06
Iodine	as barium iodide	0.03
Cesium	Molten metal ^c	0.22
Barium	As hydride ^b and iodide ^b (see iodine)	0.09
Rare Earths as Misch Metal	180 mesh powder	0.55
Uranium	200 mesh powder	remainder

^aA mixture of fission product powders and uranium powder compacted to give a dispersion of fission products within a uranium matrix.

^bMetal is subsequently liberated from hydride and iodide powders by heat.

^cThe molten cesium was mixed with uranium powder until a free flowing powder of uranium coated with cesium was obtained.

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The results of the analysis are given in Table 16 with the nominal composition of the alloy for the elements concerned. The accuracy of the analysis is an order of magnitude. This analysis confirms the presence of some of the fission constituents in concentrations about as specified.

Table 17 gives some oxygen, nitrogen, and carbon analyses for fission. The oxygen content of the fission is higher by a factor of 2 to 3 than desired, and Sylvania has been asked to lower this figure, if possible. They are attempting to locate the source of oxygen by analyses of starting uranium, powdered uranium, and hot pressed uranium, i. e., uranium without the fission elements present. The oxygen content will then be compared with that of fission to ascertain whether oxygen is being introduced via the fission product elements.

4. Extraction of Plutonium by Liquid Magnesium

Work continued in the semi-works on problems connected with isolation of plutonium from core or blanket materials by magnesium extraction. In such a process, the plutonium would be recovered from the magnesium extract by distilling the magnesium away from the extracted plutonium and any uranium which might have accompanied it.

a. Scale-Up of Magnesium Distillation Equipment (I. O. Winsch, W. H. Spicer)

A magnesium distillation unit capable of handling several kilograms of magnesium has been built to gain familiarity with this distillation operation (ANL-5466, page 56). It is planned to distill the magnesium at a temperature of around 725 C (pressure of 11 mm of mercury), and to condense it as a liquid, which will flow into a receiver.

In the past quarter, several temperature shakedown tests were made and three runs were made. The first two runs were unsuccessful because of the presence of cold spots in the condenser and liquid transfer lines, which resulted in plugging of the transfer lines and deposition of the magnesium as a solid in the condenser. Failure of a copper gasket on the condenser flange because of severe attack by magnesium also occurred in the first run. Mild steel gaskets have been used since and are satisfactory.

Alterations were made for the third run to supply additional heat to the cold spots in the system. Two kilograms of a 3-kg charge were distilled smoothly at a temperature of 725 C (pressure of 11 mm). A remaining difficulty is that magnesium solidified at the pipe opening to the receiver vessel. To remedy this, the receiver will be maintained at a temperature of around 600 C.

b. Design of Magnesium Extraction Equipment (I. O. Winsch, J. Wolkoff)

The technique of separating molten magnesium from uranium or uranium alloys after equilibration by freezing the uranium phase and

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Table 16

SPECTROSCOPIC ANALYSIS OF SYLVANIA FISSION*

<u>Element</u>	<u>Concentration in Weight Per Cent</u>		
	<u>Nominal</u>	<u>End</u>	<u>Center</u>
Silver	0.02	0.02	0.02
Aluminum	-- ^c	0.002	0.0007
Boron	-- ^c	0.00001	0.00001
Barium	0.07	0.1	0.2
Bismuth	-- ^c	0.0001	0.0001
Iron	-- ^c	0.007	0.007
Magnesium	-- ^c	0.007	0.007
Molybdenum ^a	0.16	0.1	0.1
Antimony	0.004	0.005	0.005
Tin	0.003	0.005	0.005
Strontium	0.04	0.1	0.1
Titanium	-- ^c	0.005	0.005
Zirconium ^b	0.18	0.1	0.1

^aLimit of detection 0.1^bUranium interferes^cNot added

*Analyses by Spectroscopy Laboratory of ANL Chemistry Division.

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Table 17

OXYGEN, NITROGEN, AND CARBON CONCENTRATIONS OF FISSIUM*

<u>Slug</u>	<u>Location</u>	<u>Carbon^a (ppm)</u>	<u>Nitrogen^b (ppm)</u>	<u>Oxygen^c (ppm)</u>
AF-11	End 1	81	118	430 420
AF-11	End 2	136	126	620 980
AF-7	Center	71	124	590 740

^a By combustion analysis.

^b By dissolution in hydrochloric acid and hydrogen peroxide followed by Kjeldahl analysis.

^c By conversion of oxygen to carbon dioxide and manometric measurement of volume according to procedure given in Anal. Chem., 27, 1098 (1955). Accuracy of analysis is about ± 5 per cent. Larger variations in above duplicates are probably due to inhomogeneity of fissium.

*Analyses by R. W. Bane of ANL Chemistry Division.

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pouring off the magnesium was recently investigated and summarized in the last quarterly. The amount of magnesium that remained with the uranium phase proved to be small enough not to influence presently contemplated extraction operations. This technique was therefore used as the basis for an apparatus design for carrying out a multi-stage countercurrent extraction of uranium or uranium alloys with magnesium. All stages are contained in one unit and phase transfers are made within the unit in a manner readily adaptable to remote operation. The design is now being checked for feasibility.

Design of a tantalum-lined, type 310 stainless steel batch extraction unit is almost complete.

c. Materials of Construction for Molten Uranium and Magnesium
(W. Seefeldt, L. Marek)

Testing of materials for use with molten magnesium and uranium continued. Most tests have been extended to a minimum of 24 hours to evaluate better the limitations of the tested materials. Tests with molten magnesium in iron-base alloys were made with exposure times up to 14 days. Uranium and uranium-6 per cent chromium alloys with and without magnesium were tested in tantalum. Other runs made included magnesium in molybdenum, magnesium in alumina, and magnesium plus uranium in graphite.

Several measurements of penetration rates of iron alloys by molten magnesium were conducted at 1150 C (see Table 18). Capsules were sectioned and wall thicknesses measured microscopically. In each capsule, iron dendrites were present in the magnesium phase; hence, it is probably correct to conclude that the data obtained are indicative of the corrosiveness of iron-saturated magnesium which may or may not differ from that of magnesium. In all cases the attack at the interface was more severe than liquid or vapor phase attack by factors ranging from 2 to 15. Attack above the interface by magnesium vapors was not substantially different from that below. Type 1020 steel shows evidence of being superior on this basis.

Two tests were made with magnesium in molybdenum at 700 C, one for three days, the other for six. Neither liner indicated attack--uniform or interface. Penetration rates could not be determined as the molybdenum liners were not initially uniform in cross section.

A series of four runs was made with tantalum liners: (1) uranium only, (2) uranium plus magnesium, (3) uranium-6 per cent alloy only, and (4) uranium-6 per cent chromium alloy plus magnesium. The first two were made at 1150 C, the latter two at 900 C. Efforts were made in runs (2) and (4) to create a protective magnesium barrier layer between the tantalum and uranium. This was done by heating the test capsules below the uranium or alloy melting point for 1.5 hours to encourage wetting of the tantalum by the magnesium. The technique did not accomplish the desired results. Visually, no significant attack was evident; nor were there any detectable differences between the four samples. Uniform

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Table 18

PENETRATION OF IRON-BASE ALLOYS BY MAGNESIUM AT 1150 C

Experimental Method and Equipment described in ANL-5422, page 85.

Run and Capsule No.	Metal	Exposure Time	Total Penetration, mils		
			Liquid Phase	Interface, Maximum	Vapor Phase
46-33	1020 steel	3 days	3.5	10.5	4.5
49-31	1020 steel	6 days	8.5	16.5	3.5 - 6
50-32	1020 steel	14 days	3.5 - 7.5	45	4.5 - 7.5
58-45	Type 466 Stainless	24 hours	2.5	8.5	0.5 - 1.5
59-46	Type 466 Stainless	6 days	8.5	77	2.5 - 8.5
60-47	Type 420 Stainless	24 hours	2.5 - 6.5	18	4.5 - 6.5

penetration could not be measured because of non-uniformity of cross section; however, interface attacks of 2.5 to 4 mils were noted. Additional tests will be made with capsules fabricated from flat stock to make uniform penetration measurements possible.

Graphite, in a test with molten uranium and magnesium, again failed before test completion. The failure occurred somewhere between 5.5 and 16.5 hours of exposure.

A high purity alumina (Morganite) crucible was tested with magnesium at 1150 C for 6 days. A black layer coated the crucible both inside and out and was 3.5 to 4 mils thick. A two-mil layer had formed under the same conditions in a three-day test previously reported (ANL-5466, page 61). This may be time related. No interface effects were noted.

5. Component Testing and Development

a. Development of Top Pour Uranium Melting Furnace (G. J. Bernstein, I. G. Dillon, V. N. Thelen)

Development of a suitable top pouring, uranium melting furnace continued in the past quarter. A series of six runs (9 through 14) was made in which approximately 4-kg charges of natural uranium were liquated for 4-hour periods at 1200 C before pouring. Except for run No. 9 in which the metal failed to pour and run No. 11 in which the MgO crucible cracked, the recovery of metal as ingot was about 97 per cent of that charged (Table 19).

For run No. 9, the crucible assembly was previously degassed under heat and vacuum. No explanation can be given for failure of the metal to pour. However, vacuum degassing was abandoned in favor of a simple thermal degassing at 1200 C under argon followed by cooling under argon.

The crucible assembly and tilting mechanism used was previously illustrated in ANL-5466, page 63. In the above six runs, a zirconia crucible holder was used instead of the Alfrax crucible holder shown. The crucible assembly then consisted of a heavy-walled magnesia melting crucible, a graphite crucible in which the magnesia crucible sat, and the outer zirconia crucible holder, comprised of zirconia pipe and zirconia brick insulators top and bottom. The graphite crucible acted as the induction heating susceptor and as a secondary for the magnesia crucible. A graphite pouring spout was attached to the graphite crucible.

In slagging runs using Sylvania fissium (see page 62) a relatively thick porous layer of slag has been formed on the surface of the melt. This may be troublesome in top-pouring and consequently subsequent top-pour melts will be made using fissium. For these runs, graphite crucibles coated with alumina will be used.

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Table 19

SUMMARY OF TOP-POUR CRUCIBLE RUNS

Equipment description in ANL-5466, page 63.
MgO crucible used as liner within a graphite crucible equipped with pouring spout. Four-hour liquation at 1200 C.

<u>Run No.</u>	<u>Charge (g of U)</u>	<u>Melting Time (hr)</u>	<u>Pour Temp (C)</u>	<u>Total Pour (g of U)</u>	<u>Per Cent Pour</u>
9	3397	1	1350	None	
10	4104	1	1320	3950	96.2
11	4075	1	1270	2763 ^a	68.0 ^a
12	4010	2 ^b	1320	3904	97.3
13	4002	2	1340	3912	97.7
14	4063	2	1320	3968	97.6

^a MgO crucible cracked permitting approximately 1200 g of uranium to leak into graphite mold.

^b Melting time increased to reduce thermal shock.

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b. Development of a Fusible Metal Valve
(D. C. Hampson, V. N. Thelen)

Tests of the fusible metal valve pouring method continued using alumina-coated graphite crucibles.* Ten consecutive 2-kg runs in which the metal was held molten for four hours were made in one crucible. The yield of poured metal averaged 97.5 per cent and ranged from 96 to 99 per cent. The series of runs was arbitrarily stopped after the tenth run and the slag removed. Examination of the inside of the crucible revealed that the alumina crucible had cracked at the surface of the melt. Otherwise, there were no signs of deterioration or failure of the alumina coating.

A single melt has been made consisting of fissium, the fission product concentrations being equivalent to about 1 per cent burn-up of uranium. The poured ingot was 92 per cent of the charge. A thick porous slag characteristic of fissium melts remained in the crucible. Since the crucible appeared to be suitable for re-use, a second run was made. Ingot recovery was also 92 per cent.

c. Molten Metal Sampling
(D. C. Hampson, V. N. Thelen)

A graphite, piston-type sampler was tested on molten uranium and appears to show promise. This sampler consists of a sliding plunger containing a small sample hole. The plunger is held within a graphite sleeve which seals off the sample hole during penetration of the slag into the molten metal. The melting furnace is being modified to permit testing this sampler under inert atmosphere.

d. Inert Gas Purification
(I. G. Dillon)

In a pyrometallurgical processing plant, it is currently envisioned that all operations will be conducted in an inert gas atmosphere of argon or helium. Methods of purifying these gases and of measuring the concentrations of impurities are being investigated.

An inert gas purification system has been constructed, and is now being tested. The purification system now includes a "molecular sieves" dryer and a uranium "getter" furnace for removal of oxygen, nitrogen, and water. A General Electric automatic dewpoint recorder has

*A 15 to 20 mil thick alumina coating is put on the inner surfaces of the graphite crucible and hollow leg by the Norton Co. Coating of the inner surface of the hollow leg is accomplished by splitting the leg. Splitting of the leg, however, resulted in poor coupling to an induction heater, and made it necessary to place a graphite sleeve around the leg to achieve good coupling.

been installed in this system and provides continuous measurement of the water content of the inert gases. The oxygen content of the gas may also be continuously determined as equivalent water by the method of Pepkowitz,¹⁰ which involves passing the gas, into which is introduced a small flow of hydrogen, over a heated platinum catalyst ($\sim 300^\circ\text{C}$)¹¹ to convert the oxygen to water.

In the last quarter, considerable attention has been given to studying and testing the operation of the dewpoint recorder. In this instrument, the gas is passed over a highly polished metal mirror which is cooled by mechanical refrigeration. When dew or frost begins to form on the mirror, the intensity of a beam light reflected from the mirror into a photocell is diminished. The output of the photocell is used to control a heater which raises the temperature of the mirror. At equilibrium a small spot of frost or dew is maintained in the center of the mirror. At this equilibrium condition, the temperature of the center of the mirror is taken as the dewpoint.

The range of the instrument is -100°F to $+100^\circ\text{F}$. In the range of interest, dew points of -70°F or lower, trouble has been encountered with film formation, which obscures the dewpoint or causes an instrumental response even in the absence of a frost on the mirror. The source of the film is unknown, but it frequently is attributed to oil. Trouble from this source seems to be diminishing gradually, which confirms an observation made by Pepkowitz that extensive purging of the lines and equipment seemed to be the only effective cleaning procedure.

Measurements of the oxygen and water content of several cylinders of Linde standard grade argon have been made. The argon gas as received is of high purity, as indicated by a moisture content of less than 10 ppm and an oxygen content of 5 to 10 ppm. Passage of the gas through a uranium "getter" furnace (106 grams of uranium turnings at 800°C) had little effect on total water content (initial water plus oxygen as water).

6. Design of Semi-Works Furnace Facility

Shop drawings for the improved semi-works furnace are essentially complete. This furnace will be used for handling full scale quantities of material and full scale plutonium concentrations with tracer level fission products supplemented by fissium. Design is presently underway on the ventilation system to be used with the furnace.

¹⁰Pepkowitz, L. P., Anal Chem, 27, 245 (1955)

¹¹The method of preparing the platinum catalyst is given by A. Weissberger in Physical Methods of Organic Chemistry, Vol. II, Inter-Science Publishers Inc, New York, N. Y., p. 1059 (1946)

7. Design of Pilot Plant for Processing EBR-II Fuel
by a Pyrometallurgical Process
(D. C. Hampson, J. Graae*, R. Voris**)

Work is continuing on the design of the process cell and equipment for processing the EBR-II fuel. The general building and equipment layouts are being prepared and work is progressing on design of individual equipment items and services.

*Part time, is on loan from the Lummus Company, under the Industrial Participation Program.

**Part time, is on loan from the Hercules Powder Company, under the Industrial Participation Program.

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V. FLUIDIZATION STUDIES

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(A. Jonke)

Work continued on the development of a continuous process for uranium tetrafluoride production. The effect of denitration temperature on the reactivity of uranium trioxide was studied in the fluidized bed denitrator. The product was carried through the reduction and hydrofluorination steps, and the results compared with previous runs. Other runs were made to investigate the effect of temperature during hydrofluorination and to demonstrate continuous operation in the reduction and hydrofluorination steps.

The development of a multistage, gas-solids reactor was advanced. An improved design for a gas-distributor plate was tested, and an alternative multistage design was developed.

In the waste calcination process further studies on particle growth during calcination were made. Preliminary tests on an alternative method for heating the calciner were conducted.

Fundamental studies were continued on the behavior of particles in a fluidized bed, and some preliminary correlations on particle segregation were obtained.

B. Reduction and Hydrofluorination
(N. Levitz, T. Cannon)

Previous work (ANL-5466, pages 72 to 78) had shown that the temperature at which the reduction operation was performed had a pronounced effect on the rate of the subsequent hydrofluorination reaction. A reduction temperature of about 575 C was chosen as optimum for oxide produced by fluid-bed denitration. During the past quarter additional batch runs were made to (1) investigate the effect of hydrofluorination temperature, and (2) evaluate the uranium trioxide produced by high temperature denitration. Following this work two runs were made to demonstrate continuous operation in a single stage fluidized bed.

1. Effect of Hydrofluorination Temperature

Two batch hydrofluorination runs were made in the 3-inch diameter, fluid-bed reactor using bed temperatures of 575 C in one case and 390 C in the other. The results of these runs were compared with a previous run at 450 C. The operating conditions and results for the three runs are listed in Table 20. The percentage of unconverted uranium dioxide (AOI) was 1.6 per cent at 575 C, 2.5 per cent at 450 C, and 15.4 per cent at 390 C.

The optimum temperature for hydrofluorination is, of course, dependent upon the equilibrium temperature for any given mixture of hydrofluoric acid and steam. Since in a non steady-state batch experiment, the relative amounts of steam and acid are continuously changing as the reaction proceeds, the results cannot be extrapolated to continuous operation where

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Table 20

EFFECT OF HYDROFLUORINATION TEMPERATURE ON EXTENT OF
CONVERSION IN BATCH HYDROFLUORINATION

Equipment: 3-inch diameter Monel, fluid-bed reactor

Operating Conditions

Bed Weight	6.5 to 8.5 lb UO_2
Static Bed Depth	6 to 8 inches
Gas Composition	about 60% HF, 40% N_2
HF/ UO_2 Ratio	about 2.0 x stoichiometric
Gas Velocity	0.5 ft/sec at bed conditions
Run Duration	4 hours

<u>Run No.</u>	<u>Temp (C)</u>	<u>Product Composition</u>	
		<u>AOI^a (%)</u>	<u>UF₄ (%)</u>
12A	450	2.5	98.8
15A	575	1.6	98.4
17A	390	15.4	83.3

^aAmmonium oxalate insoluble considered to be UO_2 .

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steady-state exists. The results of the batch tests are qualitatively useful in indicating that temperatures of 390 C or less are not desirable and that temperatures as high as 575 C can be used without sintering the uranium tetrafluoride.

2. Evaluation of Uranium Trioxide Produced by High Temperature Denitration

Two reduction and hydrofluorination runs were made to compare the reactivity of uranium trioxide produced by high temperature denitration (see previous section) with oxide produced at lower denitration temperatures. Reduction was performed in the usual manner for four hours at 575 C with hydrogen. The product assayed approximately 96 per cent uranium dioxide. This material was then hydrofluorinated at 450 C for four hours. The results of the two runs (18A and 19A) are given in Table 21 together with the results of two earlier runs made with oxide produced at lower denitration temperatures. By comparing the percentage of unconverted uranium dioxide (AOI) for the two runs with non-sulfated feed and likewise for the two runs with sulfated feed, it is apparent that no appreciable increase in reactivity was obtained by the higher denitration temperature.

3. Continuous Runs

Having established in previous batch tests the approximate operating conditions required, continuous runs were resumed to demonstrate the reduction and hydrofluorination steps in a single-stage fluidized bed. Reduction Run 23 was made using sulfate-activated uranium trioxide prepared in denitration Run 75. The starting bed consisted of uranium trioxide which was reduced batchwise for three hours in hydrogen. Following this initial period the trioxide was fed continuously into the top of the bed at 3.2 lb/hr and the dioxide was withdrawn from the bottom at a corresponding rate. The conditions used and the results are listed in Table 22. With an average residence time in the reactor of about 5 hours, the product assayed approximately 96 per cent uranium dioxide.

The product from the reduction run was used as feed for continuous hydrofluorination Run 16B. A starting bed of uranium tetrafluoride containing 2.43 per cent AOI was used. The feed rate was 1.98 lb/hr and the average solids residence time was 8.5 hours. The results shown in Table 23 indicate that approximately 94 per cent conversion to uranium tetrafluoride (6 per cent AOI) was attained after steady state was approached toward the end of the run. Thus in a single stage under these run conditions it is possible to produce uranium tetrafluoride which is satisfactory as feed for the production of uranium hexafluoride.

For the production of uranium metal a greater percentage conversion is required (2.0 per cent AOI). It was therefore decided to rehydrofluorinate the material from the previous run to simulate a two-stage reactor or two fluidized beds in series. In actual practice, of course, the off-gas from the second stage would be used in the first stage. This off-gas would contain a small amount of steam as reaction product, but the

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Table 21

EFFECT OF DENITRATION TEMPERATURE ON REACTIVITY
OF URANIUM TRIOXIDE

Equipment: 3-inch diameter, Monel, fluid-bed reactor.

Reduction: 4 hours at 575 C

Hydrofluorination: 4 hours at 450 C

<u>Run No.</u>	<u>Denitration Conditions</u>		<u>Hydrofluorination Results</u>	
	<u>Treatment</u>	<u>Temp (C)</u>	<u>AOI (%)</u>	<u>UF₄ (%)</u>
1A ^a	none	320	43.6	51.6
18A	none	525	32.6	64.5
12A	sulfated	310	2.5	98.4
19A	sulfated	525	8.8	86.9

^aReduction was performed at 700 C in this run.

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Table 22

SUMMARY OF CONTINUOUS REDUCTION RUN 23Equipment: 3-inch diameter, Monel, fluid-bed reactorConditions

Bed Weight	17.3 lb
Feed Material	UO ₃ from Denitration Run 75
Feed Particle Size	40 to 325 mesh
Feed Rate	3.2 lb/hr
Bed Temperature	575 C
H ₂ /N ₂ Mole Ratio	2.8
H ₂ /UO ₃ Mole Ratio	3.7
Gas Velocity	0.4 ft/sec at bed conditions

<u>Sample No.</u>	<u>Hours After Start</u>	<u>UO₂ Assay (%)^a</u>
1	1.5	96.0
2	3.0	96.8
3	4.5	96.2
4	6.0	96.2
5	7.4	95.0

^aSamples were exposed to air after cooling. A final sample maintained in a nitrogen atmosphere analyzed 97.0% UO₂.

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Table 23

SUMMARY OF CONTINUOUS HYDROFLUORINATION RUN 16BEquipment: 3-inch diameter, Monel, fluid-bed reactorConditions:

Bed Weight	16.8 lb UF_4
Static Bed Depth	approx 18 inches
Feed Material	UO_2 from reduction Run 23
Feed Rate	1.98 lb/hr
Bed Temperature	450 C
HF/ UO_2 Mole Ratio	2.4 x stoichiometric
Inlet Gas Composition	84% HF, 11% N_2 , 5% H_2
Gas Velocity	0.47 ft/sec at bed conditions
Solids Residence Time	8.5 hr average

<u>Sample No.</u>	<u>Hours After Start</u>	<u>AOI (%)</u>	<u>WS^a (%)</u>	<u>U⁺⁴^b (%)</u>	<u>UF₄ (%)</u>
1	0	2.43	0.29	75.22	96.5
2	1.5	2.64	0.34	74.85	95.7
3	3.0	2.46	0.31	75.45	96.5
4	4.5	4.49	0.30	74.65	93.4
5	6.0	3.45	0.24	74.90	94.8
6	7.5	3.91	0.22	75.10	94.6
7	9.0	4.82	0.24	75.25	93.7
8	10.5	6.73	0.14	75.55	91.9
9	12.0	5.31	0.16	75.55	93.5

^aWater Soluble — considered to be UO_2F_2 ^b100% conversion equals 75.8% U^{+4}

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amount would be sufficiently small as to have only a minor effect on the rate of reaction in the first stage. The results of the re-hydrofluorination (Run 16G) are given in Table 24. The unconverted uranium dioxide was reduced to well below the specification of 2.0 per cent AOI. A sample of the product was analyzed spectrographically for impurities. The results given in Table 25 show that the nickel content was almost twice the specification, but all other impurities are below the maximum amount permissible. It is very likely that the nickel pick-up can be reduced by a better choice of construction materials, particularly in the reduction step where Monel appears to be unsatisfactory. Corrosion will be investigated in future runs.

C. Multistage Fluidized Bed Reactor
(J. Graae, A. Jonke)

1. Solids Residence Time in Multistage Systems

Since a fluidized bed may be considered as an efficient mixing chamber, the time that any given particle of solid resides in the fluidized bed may vary from several seconds up to the length of time that the fluidized bed is in operation. If a high degree of conversion of the solids is required in a chemical reaction, then the average residue time of the solids must be sufficiently long so that only a small number of particles are in residence for less than the required reaction time. By the use of multiple stages in series the required average residence time can be considerably reduced.

The following equation¹² can be used to calculate the fraction of feed remaining in a fluidized bed system for longer than a given time if the number of stages and the overall average residence time is known. Instantaneous and homogeneous mixing is assumed.

$$N = e^{-a\theta} \left(1 + a\theta + \frac{a^2 \theta^2}{2} + \dots + \frac{a^{n-1} \theta^{n-1}}{(n-1)!} \right)$$

where N is the fraction of feed particles remaining in the system longer than time θ .

$a = \frac{1}{t_c}$ where t_c is the average residence time in each stage,

or the time required to empty a stage if the feed were stopped and the discharge rate continued unabated (equal stages assumed).

n = number of stages or vessels in series.

Calculations made with the above equation are summarized in Table 26.

¹²Kalback, J. C., Chemical Engineering 54, 136 (February 1947)

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Table 24

SUMMARY OF RE-HYDROFLUORINATION RUN 16CEquipment: 3-inch diameter, Monel, fluid-bed reactorConditions:

Bed Weight	17.4 lb UF_4
Static Bed Height	approx 19 inches
Feed Material	UF_4 from hydrofluorination Run 16B
Feed Rate	2.41 lb/hr
Bed Temperature	450 C
HF/ UO_2 Mole Ratio	1.86 (based on pure UO_2)
Inlet Gas Composition	84% HF, 9% N_2 , 8% H_2)
Gas Velocity	0.4 ft/sec
Solids Residence Time	7.2 hr average

<u>Sample No.</u>	<u>Hours After Start</u>	<u>AOI (%)</u>	<u>WS^a (%)</u>	<u>U^{+4b} (%)</u>	<u>UF_4 (%)</u>
1	1.5	3.82	0.47	76.75	96.9
2	3.0	2.39	0.32	75.25	96.5
3	4.5	0.55	0.28	74.85	98.2
4	6.0	1.55	0.22	75.50	97.8
5	7.5	1.35	0.24	75.50	98.1
6	9.0	1.17	0.24	75.60	98.4
7	10.7	1.21	0.24	74.50	97.0

^aWater Soluble — considered to be UO_2F_2 ^b100% conversion equals 75.8% U^{+4}

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Table 25

IMPURITIES IN URANIUM TETRAFLUORIDE

<u>Element</u>	<u>Analysis^a (Run 16C)</u>	<u>Specification^b</u>
Fe	5 ppm	45 ppm
Ni	80 ppm	45 ppm
Cu	15 ppm	20 ppm
Cr	1 ppm	20 ppm

^aAnalyses reported on uranium basis

^bSpecifications for St Louis Production Center
(MCW 1378, page 151)

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Table 26

EFFECT OF MULTIPLE STAGES ON REQUIREDRESIDENCE TIMETotal Average Residence Time In System = 8 hrs

<u>θ (hrs)</u>	<u>N_1^a (1 stage)</u>	<u>N_2 (2 stages)</u>	<u>N_4 (4 stages)</u>
4	0.61	0.74	0.85
2	0.78	0.92	0.98
1	0.88	0.98	

Total Average Residence Time In System = 16 hrs

<u>θ (hrs)</u>	<u>N_1 (1 stage)</u>	<u>N_2 (2 stages)</u>
4	0.78	0.92
2	0.88	0.98
1	0.94	0.99

^a N = fraction of particles remaining in system
longer than time θ

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The value of multiple stages for decreasing the average residence time is apparent from these calculations. For example, if the total average residence time is 8 hours, then the percentage of particles remaining in the system longer than two hours will be 78 per cent in one stage, 92 per cent in two stages, and 98 per cent in 4 stages.

2. Reactor Design

The problems encountered thus far in the development of a multi-stage reactor may be classified into two groups - those associated with the gas distributor plate, and those associated with the downcomers. With regard to the gas distributor plate it has been found essential that the pressure drop across the plate itself be sufficiently high that uniform gas distribution is obtained, but not so high as to require excessively long downcomers to balance the pressure drop. A porous plate gives excellent distribution but cannot be used in multistage reactors because the dust particles carried by the gas will plug the pores. In large commercial units a perforated plate is frequently used with holes of about 1/4-inch diameter spaced on 6-inch centers. With materials of high density, such as uranium oxide, the use of perforated plates was found to yield stagnant zones between the perforations extending a short distance above the plate. This could be corrected by using very small, closely-spaced holes; but again the problem of holes plugging was encountered.

In the previous report (ANL-5466, page 79) a conically shaped bed was described in which the fluidizing gas enters through a single hole at the bottom of the cone. This type of gas entry has given good fluidization for small diameters up to about 3 inches. A single cone-shaped bed does not, however, appear to be readily extrapolable to a plant-scale unit. A plate having multiple cones was therefore constructed and tested. The 6-inch diameter plate was fabricated from lucite 1 1/4 inch thick. It was drilled with 60° conical holes spaced on 1 1/4-inch centers, and tapering to a 1/16-inch diameter hole at the bottom of the plate. The cones overlap at the top of the plate, so that there are no flat surfaces for stagnant particles to collect. This plate was tested by fluidizing uranium trioxide in a glass column and was found to give excellent gas distribution. With 19 holes the pressure drop across the plate was about 1 psi at a gas velocity of 0.5 ft/sec. The same plate was tested with 1/8-inch diameter holes, but this was unsatisfactory because stagnant zones were found in a few of the cones.

Problems connected with the downcomes have been due either to bridging of solids which prevents down-flow in the tubes or to "blowing". The latter occurs when too much gas flows up the downcomer producing a gas lift which carries solids up to the stage above. To prevent "blowing", tests were made in which the downcomers were partially restricted at the bottom to limit the amount of gas entering the tubes. Such an arrangement, however, caused bridging to occur more readily. It is possible that this trouble can be avoided by increasing the downcomer diameter, and this will be studied in future experiments. Problems of this type are magnified with small-scale experimental equipment.

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If the enlargement of the downcomers is carried to an extreme, an alternative multistage design is achieved as shown in Figure 20. This design has the advantage that problems associated with downcomers are eliminated. A unit of this type having a rectangular cross section $5'' \times 2 \frac{1}{2}''$ was constructed of lucite. In preliminary tests using sand as the fluidized solids, the unit was found to operate very well. With this design the number of countercurrent stages is one-half the number of actual stages, since any molecule of gas will contact only half of the stages. Thus in Figure 20 there are only two countercurrent stages.

D. Calcination of Reactor Fuel Processing Wastes
(E. Petkus, J. Loeding, M. Jones)

In previous runs it was found that aluminum nitrate solution could be calcined to aluminum oxide in the 6-inch diameter fluid-bed calciner with no caking or other operating difficulties. It was found that particle growth was slower at an operating temperature of 450°C than at lower temperatures. During this quarter four additional runs were made to investigate particle growth, and some preliminary tests were made on an alternative method for supplying heat to the reactor.

1. Particle Growth

The operating conditions employed are listed in Table 27. Bed temperatures of 500°C or 550°C were used. The feed flow rate was approximately 2 gal/hr. In Runs 6, 7, and 8 the feed consisted of 2.2 M aluminum nitrate solution, and in Run 9 a feed was used which more nearly approximated the ICPP first cycle aqueous raffinate after concentration. Its composition was 2.1 M $\text{Al}(\text{NO}_3)_3$, 1.2 M HNO_3 , 0.15 M NaNO_3 , 0.008 M $\text{Hg}(\text{NO}_3)_2$.

To counteract particle growth, seed particles of 60 to 100 mesh aluminum oxide were fed into the reactor in two runs. The rate of seed feed was 47 per cent of the aluminum oxide production rate in Run 7 and 34 per cent in Run 9.

The results of the runs are shown in Figure 21 where the average particle diameter of samples removed at hourly intervals is plotted against the operating time. The slope of the curves represents the rate of particle growth, and it is apparent that the slope is lowest for the runs made at the highest temperatures. An operating temperature of 500 to 550°C appears to be optimum for minimum particle growth.

For the runs in which seed particles were introduced (Runs 7 and 9), an initial increase in average particle diameter occurred, followed by a leveling off, then a decrease. The initial increase was primarily due to the formation of some coarse particles larger than 20 mesh. The percentage of these particles reached an equilibrium value, thereafter remaining essentially constant. The decrease in average particle size was due to the introduction of seed particles at a rate which was greater than necessary to counteract particle growth. In fact the rate of decrease in Run 9 was so rapid that there is some doubt as to whether the seed particles are required after the initial period of about 8 hours. The difference in

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FIGURE 20
ALTERNATIVE DESIGN FOR MULTISTAGE
FLUIDIZED-BED REACTOR.

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Table 27

OPERATING CONDITIONS FOR WASTE CALCINATION RUNS

Equipment: 6-inch diameter reactor described in ANL-5290,
pages 114 to 118.

	Run Number			
	WC-6	WC-7 ^a	WC-8	WC-9 ^a
Bed Temperature, C	500	500	550	500
Fluidizing Air Flow Rate, cfm at STP	8.3	8.2	8.2	8.2
Nozzle Air Pressure, psig	33	33	32	31
Static Bed Level, inches	21	21	21	21
Feed (Aluminum-Nitrate) Concentration, <u>M</u>	2.2	2.2	2.2	2.1 ^b
Feed Flow Rate, gal/hr	2.28	2.32	1.93	2.22
Run Duration, hr	14.5 ^c	14 ^c	7	21 ^c

^aAluminum oxide seed particles introduced during these runs.

^bFeed contained in addition 1.2 M HNO₃, 0.15 M NaNO₃, 0.008 M HG (NO₃)₂.

^cRuns made in 7-hr periods with overnight shutdown between periods.

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FIGURE 21
 RATE OF PARTICLE GROWTH IN
 WASTE CALCINATION RUNS.
 (for complete run conditions see Table 6)

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particle growth behavior in Run 9 as compared to previous runs may be due to the different feed composition used in this run.

Differences were also noted in the bulk density and nitrate content of the aluminum oxide from Run 9 as compared to the runs made with pure aluminum nitrate solution. The bulk density of the oxide from Run 9 was about 1.2 g/cc, and the residual nitrate content was 2.1 per cent. For the oxide from previous runs the bulk density was about 0.7 g/cc and the nitrate was less than 1 per cent.

2. Alternative Heating Methods

In the 6-inch diameter calciner, heat is supplied through the reactor wall by means of electric heaters in contact with the exterior wall surface. In a plant-scale calciner the wall area available for heat transfer would be limited, and a portion of the heat would have to be supplied by other means. One method would be to install electric heaters inside the reactor in the fluidized bed. A second possible method, which might have the advantage of greater simplicity and ease of maintenance, would be to inject a liquid hydrocarbon fuel directly into the hot bed where oxidation and liberation of heat would occur. This technique is used commercially for the calcination of limestone, oil being used as the fuel.

To test the technique, kerosene was chosen as the fuel because of its low ignition temperature (295 C). The kerosene was fed at the rate of 10 to 20 ml/min through a spray nozzle into a bed of aluminum oxide fluidized with air and preheated to 500 C. The occurrence of a reaction was evidenced by an increase in the bed temperature to about 550 C, but the heat liberated was only a fraction of the theoretical heat value of the kerosene fed. It was concluded that incomplete combustion of the fuel had occurred.

The above test was repeated in the same manner except that aluminum nitrate solution was fed into the bed through another nozzle at the same time as the kerosene. It was hoped that the nitrate from the feed would cause more rapid oxidation of the kerosene than air alone. The results, however, were similar to those of the first test. In addition it was noted that the condensate from the off-gas condenser had an odor resembling nitroparaffins, indicating that the kerosene was not completely oxidized.

3. Calcination of Active Waste Solutions

The design of a fluidized-bed calciner capable of operating with radioactive feeds has been started. This unit, which will be similar to the existing calciner, will be installed in a shielded cell and will be operated remotely. Progress on the design of this unit will be reported at a later date.

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E. Fundamental Fluidization Studies
(H. Katz, T. Cannon)

Studies of particle size distribution in fluidized beds of wide particle size range have been continued. The experimental technique finally adopted for these studies is as follows. A mixture of glass beads of known particle size distribution is poured into a long plexiglass column two inches in diameter and fluidized for several minutes at an air flow rate sufficiently high to insure complete mixing. The flow thru the bed is then shut off rapidly by shunting the air thru a by-pass line just below the column entrance. The flow rate is then adjusted to the desired value and the bed fluidized for half an hour. Experiment showed that under some conditions the two-minute period previously used was not long enough for an equilibrium distribution to be reached. At the end of half an hour, the air is again shut off rapidly and a hot gelatine solution carefully poured into the bed. The column is then jacketed with crushed dry ice until the bed is frozen. It is then removed and sliced into sections of the desired length with a hot wire glass cutter. Finally, each section is washed with hot water to remove the gelatine, and the beads are filtered, dried, and screened. Since preliminary experiments indicated that better reproducibility could be obtained with deeper beds than the three-inch beds originally used, a fixed bed height of about six inches was adopted for all runs.

The reproducibility of data obtained by this procedure is satisfactory, as shown in Figures 22 and 23 in which the results of replicate runs at three different fluidizing velocities are plotted as weight per cent of coarse (20-40 mesh) beads in each section versus the mid-height of the section above the bottom of the bed. In all cases, material balances checked within two per cent. These data showed that appreciable classification of particles occurred in the fluidized bed at low gas velocities. At higher velocities the particle distribution became more nearly uniform except at the very bottom of the bed where coarse particles tended to concentrate.

In order to establish the minimum fluidizing velocities for the coarse beads and the fine beads as well as for mixtures of the two sizes, a series of pressure drop measurements was made at various gas flow rates. These results are shown in Figure 24 in which the pressure drop is plotted against mass flow rate of the gas. For the narrow cuts (140 to 200 mesh and 20 to 40 mesh) the curves have the usual characteristic shape. The curves for the mixtures of fine and coarse beads, however, exhibit some interesting characteristics, not previously recognized. Referring to Figure 24 at flow rates below point A, there is no particle movement and the usual fixed bed relationship applies. Between A and B, there is slight expansion and rearrangement, with some segregation of the large particles. This is an unstable region, showing poor reproducibility. In the linear region from B to C, the bed consists of two distinct sections. The bottom section, consisting mainly of larger particles, is static, with virtually no particle movement. The upper section, mostly fine particles, is completely fluidized. The interface between the two sections is well defined, and data in this region are easily reproducible.

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FIGURE 22

DISTRIBUTION OF PARTICLES IN A FLUIDIZED
BED CONSISTING OF A MIXTURE OF
COARSE AND FINE PARTICLES.
(starting mixture - 66% 20-40 mesh, 34% 140-200 mesh)

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FIGURE 23
DISTRIBUTION OF PARTICLES IN A FLUIDIZED
BED CONSISTING OF A MIXTURE OF
COARSE AND FINE PARTICLES.

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FIGURE 24.
RELATIONSHIP BETWEEN PRESSURE DROP
AND GAS FLOW RATE FOR VARIOUS
MIXTURES OF GLASS BEADS.

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As the flow rate is increased from B to C, the length of the fixed bed section decreases, and that of the fluidized section increases. Finally, at point C the fixed section disappears and the bed is completely fluidized. Thus the minimum fluidizing velocity for these mixtures is not clearly defined, since fluidization starts at point A but is not complete until point C is reached. It is of interest to note that excellent quality of fluidization is obtained in the upper section in region B-C, indicating that a fixed bed is an excellent gas distributor for fluidization.

On the pressure drop curves the region from B to C was of particular interest, and it was decided to concentrate further work on flow rates corresponding to point B and higher. It was also deemed desirable, in the region B-C, to slice the bed at the interface of the fixed and fluidized sections, and then subdivide each of these, instead of taking cuts of arbitrary uniform length as was done in earlier runs. This new procedure was followed in the next set of runs, shown in Figure 25.

Examination of the data shown in this figure reveals that for the mixture used (20% coarse and 80% fine beads) the distribution of particles varied greatly with gas velocity. At low gas flows (19.0 lb/(hr)(sq ft)) corresponding to a point slightly above B on the pressure drop curves, the upper fluidized section of the bed consisted entirely of fine beads and the lower static bed was a mixture of fine and coarse beads. At a higher gas velocity (35.9 lb/(hr)(sq ft)) corresponding to a point slightly below C, the upper fluidized section was predominantly fines with a very small percentage of coarse beads, and the static section was predominantly coarse beads with a small percentage of fines. At the highest gas velocity (55.8 lb/(hr)(sq ft)) corresponding to a point above C, the particle distribution was very nearly uniform except for a very short section at the bottom of the bed. This concentration of coarse material at the bottom may be due to rearrangement of the gas flow pattern and velocity as it leaves the porous plate distributor.

In the region B-C, it is planned to correlate the data as follows. From Figure 22 and 23, it appears that the data in this region can be fairly well represented by two horizontal lines, representing the compositions of the fixed and fluidized sections. From the measured height and weight of the fixed bed section, and knowing the particle and fluid properties, it is possible to calculate some average particle size from the Carman-Kozeny¹³ equation. If this particle size can then be related to the composition of the fixed bed section, the composition of the fluidized bed section can be calculated by material balance. If this method proves feasible, it will be possible to calculate the composition of each section without the tedious procedure of freezing and slicing

¹³Leva, M., Grummer, M., Weintraub, M. and Polchik, M., Chem. Eng. Progress 44, 511 (1948)

FIGURE 25

DISTRIBUTION OF PARTICLES IN A FLUIDIZED
BED CONSISTING OF A MIXTURE OF
COARSE AND FINE PARTICLES.

(starting mixture - 20% 20-40 mesh, 80% 140-200 mesh)

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the bed. A pressure probe could be inserted at the interface and the pressure drop across the fluidized section measured. Since this pressure drop is essentially equal to the bed weight divided by cross sectional area, the weight of the fluidized portion can be calculated and the weight of the fixed section obtained by difference. Thus it would be possible to calculate the particle size distribution in a bed from only bed height and pressure drop measurements.

The procedure has been attempted with some of the present data and work is currently being directed toward deriving a relationship between average particle size calculated from the Carman-Kozeny equation and actual bed composition in terms of screen size openings.

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VI. REACTOR CHEMISTRY AND OTHER PROBLEMS

A. Breeding Gain Determination(C. E. Crouthamel, P. Kafalas, E. Rathbun, M. Laug,
R. Heinrich)

The determination, by chemical analysis, of the conversion ratio or breeding gain of the EBR under various circumstances is the objective of this program. The breeding gain of the reactor with a plutonium loading is next to be determined. The burn-up determination of the core material requires a calibration experiment using plutonium to correlate the number of fission events with the formation of fission activity. The experimental approach has been described in ANL-5388, page 76, ANL-5422, page 114, and ANL-5466, page 86.

Preparations for the fission calibration experiment have been essentially completed. Tests of the operating shields at the pile for the protection of personnel indicated that the neutron and gamma leakage through the shielding was negligible. The electronic circuits to be used for the fission counting have been built. The operation of these circuits has been tested with a one-gram Ra-Be neutron source. The pulses from the fission chamber have been analyzed with a single channel analyzer to determine how well the system can distinguish between a high alpha background and low-energy fission fragment pulses. Similar tests will be carried out at CP-5 under conditions identical to those to be encountered in the actual experiment.

After the equipment has been operated successfully and is in its final form it will be described in detail.

B. Metal Oxidation and Ignition

(R. C. Vogel, H. A. Porte, J. G. Schnizlein)

It is generally known that many spontaneous ignitions of uranium, zirconium, thorium, and plutonium have occurred. The ignitions have occasionally taken place in metal initially at room temperature and even in apparently bulk metal. The frequency of these ignitions is great enough to constitute a serious hazard. A study of the circumstances surrounding each ignition did not definitely indicate the causes. It has, therefore, been necessary to undertake a basic laboratory investigation.

In a much oversimplified manner the mechanism of spontaneous metal ignition will be hypothesized. Consider a bulk piece of metal which has certain surface irregularities leading to high surface area. The metal irregularities will eventually suffer accelerating oxidation or ignition if the rate of heat liberation due to metal oxidation is greater than the rate of heat loss. When this occurs the bulk metal in addition to the surface irregularities may be completely oxidized. Let us consider the general factors influencing the rates of heat liberation and loss.

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<u>Step</u>	<u>Possible Factors Influencing Rate</u>
Metal surface of unit area oxidizing in air.	<ol style="list-style-type: none"> (1) Metal purity. (2) Metallurgical condition (grain size, strains, etc). (3) Temperature. (4) Time. (5) Gas Composition. (6) Type of oxide film formed (protective or not).
Loss of heat of reaction by conduction to surroundings.	<ol style="list-style-type: none"> (1) Thermal conductivity of metal. (2) Thermal conductivity of oxide coating. (3) Cross sectional area at right angles to direction of heat flow. (4) Temperature gradient.

In order to understand the causes of metal ignitions it is necessary to isolate the variables and study them separately. If one studies the rate of oxidation of polished flat specimens under isothermal conditions it is possible to study the variables of metal purity, metallurgical condition, temperature, gas composition and type of oxide film without the difficulty of variable surface area. Another approach is to prepare powders, perhaps by hydriding and dehydriding, and then to measure the surface area. This is an approach which may be taken later. It does not seem as attractive at this time since (1) hydrogen in the metal may be a pertinent variable at least in the case of uranium, (2) the experiments involved a surface area measurement, (3) it is difficult to guarantee that a sample of powder is isothermal and (4) it is difficult to measure the true temperature of a powder.

It has, therefore, been decided to study the factors influencing the rate of oxidation of polished pieces of uranium, zirconium, thorium, and plutonium. These studies will be carried out from room temperature up to the temperature of self sustaining oxidation (ignition) for the bulk metal samples. The studies will be started with uranium.

A literature search has been made of the available data on the oxidation of uranium. The information available in the literature has been plotted as weight gain per unit area against time for various temperatures in Figures 26, 27, and 28. Figure 26 shows the available data in the temperature range up to 100 C, Figure 27 shows the available data from 100 to 200 C, and Figure 28 shows the available data at temperatures above 200 C. It is clear that there is a considerable spread of the data. For example, at 100 C and after 4000 minutes the extent of oxidation for various experiments under similar conditions varies by about a factor of forty. At 200 C and after 40 minutes the extent of oxidation varies by a factor of twenty for similar experiments. Rather modest differences in rate could make the difference between the usual slow corrosion and ignition (too rapid in oxidation for heat loss to maintain isothermal conditions);

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FIGURE 26

SELECTED LITERATURE DATA ON OXIDATION OF URANIUM, 20 TO 100 C.

Total Pressure 1 atm unless otherwise indicated.

(1)	O ₂	D. Cubicciotti	J.A.C.S. <u>74</u> , 1079 (1952)
(2)	Air	J.G. Thompson	N.B.S. CT-1006, CT-2733 (1945)
(3)	O ₂	J. Loriers	Compt. Rend. <u>234</u> , 91 (1952)
(4)	Air	R. Hellyer	Poc-mem 16, (1948)
(5)	Air	Covert and Kolodney	LA-313 (1945)
(6)	Air	T. Wathen	BR-223 (1943)
(7)	O ₂	K.T. Perkins	CT-1008 (1943)
(8)	Air	J.T. Waber	LA-1524 et al (1952)
(9)	Air	H. Greenwood	ME-24 (1943)

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FIGURE 27

SELECTED LITERATURE DATA ON OXIDATION
OF URANIUM, 100 TO 205 C.

Total Pressure 1 atm unless otherwise indicated.

(1)	O ₂	D. Cubicciotti	J.A.C.S. <u>74</u> , 1079 (1952)
(2)	Air	J.G. Thompson	N.B.S. CT-1006, CT-2733 (1945)
(3)	O ₂	J. Loriers	Compt. Rend. <u>234</u> , 91 (1952)
(4)	Air	R. Hellyer	Poc-mem 16, (1948)
(5)	Air	Covert and Kolodney	LA-313 (1945)
(6)	Air	T. Wathen	BR-223 (1943)
(7)	O ₂	K. T. Perkins	CT-1008 (1943)
(8)	Air	J. T. Waber	LA-1524 et al (1952)
(9)	Air	H. Greenwood	ME-24 (1943)

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FIGURE 28.

SELECTED LITERATURE DATA ON OXIDATION
OF URANIUM, 200 C AND HIGHER.

Total Pressure 1 atm unless otherwise indicated.

(1)	O ₂	D. Cubicciotti	J.A.C.S. <u>74</u> , 1079 (1952)
(2)	Air	J.G. Thompson	N.B.S. CT-1006, CT-2733 (1945)
(3)	O ₂	J. Loriers	Compt. Rend. <u>234</u> , 91 (1952)
(4)	Air	R. Hellyer	POC-Mem 16, (1948)
(5)	Air	Covert and Kolodney	LA-313 (1945)
(6)	Air	T. Wathen	BR-223 (1943)
(7)	O ₂	K.T. Perkins	CT-1008 (1943)
(8)	Air	J.T. Waber	LA-1524 et al (1952)
(9)	Air	H. Greenwood	ME-24 (1943)

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therefore, it is appropriate to investigate the causes of these differences.

It has been difficult to evaluate the data in the literature on the oxidation of uranium since in most cases important experimental details have been omitted. In the earlier reports there is an almost universal omission of any information concerning the source and metallurgical history of the uranium samples used. In many instances no attempt has been made to assess the purity of the metal. It is not inconceivable that the rather large discrepancies in the rates found by various investigators were caused by differences in the purity and physical properties of the metal rather than being due entirely to the variations in the experimental methods involved.

In studies of the oxidation to be conducted here it is planned to maintain careful control of the variables of trace impurities in the metal, metallurgy, and minor constituents of the gas and to determine which may be the most important in controlling the abnormally high pyrophoricity of these metals.

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VII. ANALYTICAL RESEARCH AND SERVICE WORK-SOLVENT

EXTRACTION OF MOLYBDENUM

(C. E. Crouthamel, L. E. Trevorrow)

Solvent extraction methods were investigated as a means of separating molybdenum from fission product mixtures for radiochemical analysis. Experiments were performed using tracer techniques on Mo⁹⁹ in the presence of molybdenum carrier.

Molybdenum was extracted from acid molybdate solutions into various solvents. Several systems were shown to be more efficient than the classical extraction of Mo(VI) from hydrochloric acid solution into diethyl ether. Many of these have been reported just recently.¹⁴ However, the most efficient methods for molybdenum are also favorable for the extraction of uranium. Typical of these are the distribution between hydrochloric acid solutions and hexone or tri-n-butyl phosphate.

A method for molybdenum which has neither been widely used nor studied in detail is the extraction of the metal xanthate into chloroform.^{15,16} This procedure promises to suit the present purpose since it is both efficient and, to a certain extent, specific for molybdenum. Experiments were performed to determine the effect on this extraction of shaking time, acidity of aqueous phase, various anions, and initial mole ratio of xanthate to molybdenum. It was found that 98 per cent of the molybdenum could be extracted in the first step with a shaking time of only two minutes. Experiments conducted thus far suggest the following conditions for the most efficient isolation of molybdenum using the xanthate extraction. The initial hydrochloric acid molarity should be about 0.5 M in the aqueous phase. The xanthate concentration should be at least 12 times the molar concentration of molybdenum.

¹⁴Nelidow, I., and Diamond, R. M., J Phys Chem, 59, 710-18 (1955)

¹⁵Malowan, S. L., Z anorg allgem Chem, 108, 73 (1919); Z anal Chem, 79, 202 (1929) (via E. B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc)

¹⁶Geilman, W., and Bode, H., Z anal Chem, 128, 495-507 (1948)

The addition of potassium ethyl xanthate solution to the acidic molybdenum(VI) solution should be immediately followed by extraction of the mixture with chloroform. No pre-equilibration of the chloroform with a corresponding aqueous solution is necessary. One experiment was performed with a uranium(VI) solution under conditions most favorable for the separation of molybdenum from uranium by the xanthate extraction of molybdenum. The distribution ratio (A/O) for uranyl ion was 500 or greater. This method appears promising as a separation of molybdenum from uranium.

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VIII. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste Processing Operations(J. F. Harast, A. C. Rashinskas, K. O. Bremer, W. Palmer,
M. Deerwester)

The total volume of liquid radioactive wastes processed was 55,000 gallons during the period June 18 through September 30. This represented 34,000 gallons from retention tanks and decontaminating solutions from the Reclamation Department, 11,000 gallons of "pool" water from the gamma irradiation facility and 10,000 gallons of miscellaneous wastes. There were 1053 retention tanks sampled and 31 were sent to Building 310 for processing, or 2.9 per cent. Seven had to be processed due to over-tolerance strontium-90, 21 due to high alpha activity and the remaining 3 because of gross counts.

B. Waste Processing Laboratory

(R. A. Juvinall, J. Vincenzi, A. S. Porter)

Pool water from the gamma irradiation facility reached an activity level of 7600 cpm/ml (50 per cent geometry) on September 7. The pH of the pool water varied between 7.6 to 7.9 and the total solids were 540 ppm. A cation exchanger was found to be ineffective for removing the activity, which, according to a gamma scan was mainly Zn^{65} . A dual and a mixed bed exchanger were both effective in removing the activity and the breakthrough point came at about 1000 gal per cu ft of mixed resins for each.

C. Gamma Irradiation Facility(J. F. Harast, R. A. Juvinall, W. H. Kline, A. C. Rashinskas,
W. Palmer, R. Thurnblad, J. Vincenzi, R. Testin, H. Turner)

The first samples to be irradiated in the new facility (see Figure 29 for a view of the irradiation rack taken through the shielding water.) were powdered milk for the Quartermaster Food and Container Institute on August 5. Through the end of September (September 30), a total of 1139 samples have been irradiated. Most of the samples have been foods but in addition there have been chemicals or chemical products. Most of the samples have come from contractors with the Quartermaster Food and Container Institute but there have been a few directly from private industry.

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Figure 29 - Irradiation Facility

View of irradiation rack taken through 15 feet of shielding water.

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There were only eight fuel rods in the rack from July 29 to September 6. During this period a thorough check of the intensity in each of the sample ports was made using ferrous-ferric dosimetry. Dosimetry measurements are taken in glass cells which are centered inside of No. 2 cans (Figure 30). The cans are then filled with distilled water, put in the urn and lowered into the gamma rack by means of a cable on a winch. In ferrous-ferric dosimetry the solution used is 0.001 M ferrous sulfate and 0.001 M sodium chloride in 0.8 N sulfuric acid. The solution is read directly in a Beckman DU spectrophotometer in the ultraviolet region at a wave-length 3020 Å, and at a temperature of 25 C. The calibration curve for ferric ion at 25 C is shown in Figure 31.

The ferrous dosimetry was checked against the ferrous-cupric dosimetry of Hart.¹⁷ In this method the solution is 0.001 N FeSO_4 , 0.01 M CuSO_4 in 0.01 N sulfuric acid. The G-factor for this solution is 0.66, i.e. 0.66 molecule of iron is oxidized per 100 e.v., whereas the ferrous dosimetry, 15.6 molecules of iron are oxidized per 100 e.v. The results between the two methods were found to agree within ± 1 to 2 per cent.

Since the gamma source uses spent fuel rods from the MTR reactor, decay curves have been plotted to show the slope of the curves for each position in the rack as well as in the five possible positions within the urn. These results are shown in Figure 32.

As the intensity of the source was falling below one million r/hour, four new fuel rods were requested. These were received on September 6 and it is now possible to irradiate samples in six urns surrounded by four fuel elements instead of three urns as previously.

The "pool" water was originally ANL tap water to which had been added 200 ppm sodium nitrate as a corrosion inhibitor, and the pH of the water was adjusted to 8.5 with nitric acid. ANL tap water has a pH of 9 to 9.5. Daily tests were made of the water for activity, pH, residual chlorine, chloride ion and occasional tests were made of the nitrate content. As time went on the activity of the water increased until on September 7, 1955, it reached 7600 cpm/ml (50 per cent geometry). Solids in the water started precipitating out and the rack started to corrode. It was then decided to demineralize the water and a 100,000-grain capacity mixed bed ion-exchange unit was purchased. The resins used are a 2:1 ratio of Nalcite SAR- OH^- to Nalcite HCR- H^+ . The activity has now been reduced to 350 cpm/ml.

¹⁷Hart, E. J. and Walsh, P. D., "A Molecular Product Dosimeter for Ionizing Radiations," Radiation Research 1:342 (August, 1954)

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Figure 30 - Glass Cell in No. 2 Can

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FIGURE 31.
CALIBRATION CURVE FOR FERROUS DOSIMETRY
AT 25 C.

FIGURE 32.
FISSION PRODUCT DECAY CURVES IN r/hr IN ANL GAMMA
IRRADIATION FACILITY WITH 8 MTR FUEL RODS
IN RACK AS DETERMINED BY FERROUS-FERRIC DOSIMETRY.

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