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ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 13. Pilot-plant Studies of the Fluorination of Uranium Oxide with Bromine Pentafluoride

by

John T. Holmes, Lowell B. Koppel,
N. Saratchandran, James B. Strand,
and D. Ramaswami

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Chemical Separations
Processes for Plutonium
and Uranium

ARGONNE NATIONAL LABORATORY

9700 South Cass Avenue

Argonne, Illinois 60439

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Chemical Engineering Division

May 1968

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SUMMARY

Engineering-scale studies were performed in a 3-in.-diam fluid-bed reactor facility to determine the effects of important process variables on the oxidation of crushed UO_2 pellets to U_3O_8 fines in an oxygen-nitrogen stream and the subsequent fluorination of the U_3O_8 with BrF_5 diluted with nitrogen. A fluidized bed of inert alumina served as a heat-transfer medium for the exothermic chemical reactions. The work with BrF_5 consisted of a fractional factorial experiment of eight runs to determine the effects of six process variables on UF_6 production rate, BrF_5 utilization efficiency, and the reaction-rate constant.

Crushed UO_2 pellets were oxidized at 450°C using 19.2 v/o oxygen in nitrogen. A larger charge of UO_2 (4.4, rather than 2.2 kg) and finer alumina (-100 nominal mesh, rather than -48, +100 mesh) increased the average oxidation rate slightly. The presence of inactive fission-product compounds did not affect the oxidation rate.

In the fluorination of the U_3O_8 fines with BrF_5 , the higher temperature (300 , rather than 225°C), the higher inlet partial pressure of BrF_5 (~ 0.29 , rather than ~ 0.16 atm), the greater superficial-gas velocity (0.89 , rather than 0.53 ft/sec), and the larger amount of UO_2 charged to the reactor had positive effects on (increased) the UF_6 production rate. The higher temperature and the greater amount of UO_2 charged to the reactor increased the BrF_5 utilization efficiency. Favorable conditions (within the ranges studied) for the BrF_5 fluorination are: a temperature of 300°C , an inlet BrF_5 partial pressure of 0.29 atm, a fluidizing-gas velocity of 0.89 ft/sec, and a UO_2 charge of 4.4 kg. The use of 48 to 100 or -100 mesh alumina and the presence of fission-product compounds did not significantly affect these results. Although no runs were made at the favorable combination of conditions, the expected average UF_6 production rate and average BrF_5 utilization efficiency for fluorinating the first 50% of the uranium are 185 lb/(hr)(ft²) of UF_6 and 75%, respectively. These results are considered acceptable for process application.

I. INTRODUCTION

Fluid-bed fluoride-volatility processes for the recovery of uranium and plutonium from spent, low-enrichment uranium dioxide fuels for power reactors are being developed at Argonne National Laboratory. The investigation described in this report pertains to a process having the following cycle:

1. Oxidation of $\text{UO}_2\text{-PuO}_2$ with 20 v/o O_2 at 450°C to form $\text{U}_3\text{O}_8\text{-PuO}_2$ fines.
2. Fluorination of $\text{U}_3\text{O}_8\text{-PuO}_2$ with BrF_5 at $200\text{-}400^\circ\text{C}$ to form volatile UF_6 and solid PuF_4 .
3. Recovery of plutonium as volatile PuF_6 by fluorinating the PuF_4 with elemental fluorine at $250\text{-}550^\circ\text{C}$.

This process is an alternative to one in which fluorine is the sole fluorinating agent.

The experiments reported here are concerned with only the first two steps of the process. Therefore, UO_2 rather than $\text{UO}_2\text{-PuO}_2$ was used as the feed material.

Bromine pentafluoride produces several desirable results when it is used as a fluorinating agent for uranium. Fluorination with BrF_5 completely separates uranium from plutonium, since BrF_5 selectively fluorinates uranium oxide to volatile UF_6 and converts plutonium oxide to nonvolatile PuF_4 . The plutonium can subsequently be recovered as PuF_6 by fluorination with elemental fluorine. The use of BrF_5 as the initial fluorinating reagent results in high production rates of UF_6 , $>170 \text{ lb/}(\text{hr})(\text{ft}^2)$, compared with direct fluorination with fluorine, $\sim 80 \text{ lb/}(\text{hr})(\text{ft}^2)$. The once-through utilization efficiency of BrF_5 is as high as 80% during the period when most of the uranium is volatilized. Operational problems such as bed sintering and poor temperature control have been essentially eliminated by the use of BrF_5 rather than fluorine for the fluorination of uranium oxide.

Jarry and Steindler¹ summarized the stoichiometry and kinetics of the reaction of BrF_5 with U_3O_8 . They showed the stoichiometry to be

UO_2F_2 and UF_4 are probable intermediates, and BrF_3 is a possible minor product. Jarry and Steindler characterized the kinetics of the reaction by the equation

$$\log k' = 0.9 \log P - \frac{2000}{T} + 0.22,$$

where P is in Torr; k' , the diminishing sphere rate constant,² is in min^{-1} ; and T is in degrees, Kelvin. The activation energy was measured to be 9.2 kcal/mole. The data were obtained in thermobalance experiments.

Bench-scale studies by Gabor and Ramaswami³ determined the feasibility of using this reaction scheme for fluorinating uranium oxide in a 1.5-in.-diam fluid-bed reactor. The conclusions of Ref. 3 were:

- "1. The lowest fluorination temperature with BrF_5 for practical operation is 200°C .
2. The rate of fluorination increases with the concentration of BrF_5 in the range of 10 to 50 v/o BrF_5 in nitrogen.
3. Direct fluorination of UO_2 pellets with a mixture of 10 to 20 v/o BrF_5 and 30 v/o oxygen in nitrogen at 300 to 400°C essentially does not proceed.
4. A small concentration of BrF_5 (1 to 2 v/o) acts as a promoter for fluorination of U_3O_8 with elemental fluorine at low temperatures ($\sim 200^\circ\text{C}$).
5. A 3-hr run, consisting of alternate oxidations and fluorinations, results in a slight increase in oxidation of UO_2 to U_3O_8 fines and a slight decrease in the fluorination of the U_3O_8 to UF_6 , in comparison to another 3-hr run consisting of 1 hr of oxidation followed by 2 hr of fluorination.
6. The fluorination with BrF_5 proceeds smoothly in a fluid-bed reactor. No bed caking was observed in any of the runs."

Anastasia⁴ studied the entire process cycle in a bench-scale (2.0-in.-diam) fluid-bed reactor. Examining the effect of temperature during reaction at 200, 250, 300, 350, and 400°C using 10 v/o BrF_5 , Anastasia found that the average production rates of UF_6 at these temperatures were 14, 27.7, 40-45, 39, and 44 $\text{lb}/(\text{hr})(\text{ft}^2)$, respectively. The average BrF_5 utilization efficiencies were 8, 16, 28-37, 32, and 38%, respectively. This observed temperature effect compared well with that measured by Jarry and Steindler.¹

Anastasia⁴ obtained higher production rates of UF_6 and higher BrF_5 utilization efficiencies at the higher temperatures, but found that the uranium fluorination temperature affects subsequent plutonium removal from the bed. Following a BrF_5 fluorination at 200°C and a plutonium-volatilization step, plutonium concentration in the final alumina bed was 0.007 w/o. When the U_3O_8 - BrF_5 reaction temperature was increased to 400°C , the plutonium retention in the final bed was 0.014 w/o. However, plutonium retention in the bed is sufficiently low when the U_3O_8 - BrF_5 reaction is carried out at 250 - 350°C .

Parallel studies with ClF_3 have been carried out on fast-reactor fuels at Centre d'Etude de l'Energie Nucleaire (CEN), Mol, Belgium.⁵ Results of this work indicate that:

1. Uranium dioxide pellets readily react with ClF_3 . Demonstration experiments in a fluid-bed reactor (using a pellet depth of 1 m) yielded a reaction rate for UF_6 of 98.8 lb/(hr)(ft²) and an average ClF_3 utilization efficiency of 81% when 25 v/o ClF_3 was fed at 6-cm/sec gas velocity.

2. Laboratory experiments have shown that at 225-500°C and with a ClF_3 concentration of 30-70 v/o, ClF_3 cannot be used for selectively volatilizing uranium, since under these conditions PuF_4 reacts with ClF_3 , forming volatile PuF_6 . Use of equimolar mixtures of Cl_2 and ClF_3 suppresses the volatilization of plutonium.

Other studies included conversion of U_3O_8 to UO_2F_2 and UF_4 by hydrofluorination prior to uranium volatilization. Reaction of mixtures of UO_2F_2 and UF_4 with equimolar mixtures of ClF_3 and Cl_2 yielded very high reaction rates--comparable to reaction rates with pure ClF_3 . It was also found that ClF reacts with U_3O_8 , forming volatile UF_6 , and that ClF suppresses the volatilization of plutonium.

This report summarizes an engineering-scale study of the BrF_5 fluorination of U_3O_8 fines in a 3-in.-diam fluid-bed reactor. As part of this study, the U_3O_8 was produced in the fluid-bed reactor by oxidation of UO_2 pellets that were fragmented to simulate discharged reactor fuel, and this U_3O_8 was subsequently used as a feed for the fluorination step. Results from this oxidation step are presented. Appendix A is a detailed literature survey of the chemical pulverization of UO_2 .

The objectives of this work were to:

1. Determine the effects of six process variables on the UF_6 production rate, BrF_5 utilization efficiency, and rate constants to provide data for the selection of the best procedure for fluorinating U_3O_8 with BrF_5 .
2. Demonstrate the feasibility and reliability of fluorinating large quantities (i.e., deep beds) of U_3O_8 fines with BrF_5 .
3. Develop continuous methods for monitoring the progress of the fluorination of U_3O_8 with BrF_5 .
4. Determine the effects of some of the process variables in the oxidation step.

II. EQUIPMENT, INSTRUMENTATION, AND OPERATING PROCEDURES

A. Equipment

The major equipment items used in this study were: (1) A preheater to heat the reagent gases to operating temperatures; (2) a fluid-bed reactor, which consists of (a) a reaction section to contain the fluidized bed and fuel charge and (b) a filter and disengaging section to prevent entrained solids from entering the off-gas lines; (3) sodium fluoride traps to sorb UF_6 from the off-gases; and (4) a scrubber system to remove interhalogens and untrapped UF_6 from off-gases leaving the sodium fluoride traps. Table I summarizes the sizes and materials of construction of this equipment, and Fig. 1 is a schematic diagram of the fluorination facility. Corrosion rates of some nickel equipment are given in Appendix B.

TABLE I. Equipment Specifications

Item	Size	Material
Preheater	3-in. diam, 27-1/2 in. long	Schedule 40 nickel pipe
Fluid-bed Reactor		
Reaction Section	3-in. diam, 72 in. long	Schedule 40 nickel pipe
Filter Section	11-in. diam, 36 in. long, 1/8-in. wall	Nickel
Sintered-metal Filters	3 in. wide, 18 in. long (bayonet type)	Two are 10- μ pore-diameter Monel, and two are 5- μ pore-diameter nickel.
Large NaF Traps	6-in. diam, 21 in. long	Monel
Small NaF Traps	4-in. diam, 24 in. long	Copper
Off-gas Scrubber	8-in. diam, 90 in. long	Schedule 80 nickel pipe

1. Preheater

The preheater section is a Schedule 40 nickel pipe, 3 in. in diameter and 27 $\frac{1}{2}$ in. long, filled with 3/8-in.-diam nickel spheres and heated by three 1000-W, 230-V tubular heaters.

2. Reaction Section of Reactor

A 3-in.-diam, 72-in.-long Schedule 40 nickel pipe is the reaction section, which contains the fluidized bed and fuel charge. It is fitted with 11 ports on each side, 6 in. apart, for thermowells, pressure taps, or bed sampling ports. Heating and cooling are separately controlled in four equal sections along the length of the reaction section. Heat is provided by twenty-four 1000-W, 120-V coiled tubular heaters. Similarly, cooling is provided by a solenoid-controlled air-water mixture passing through 24 coils of stainless steel tubing. Both the heating and cooling coils are covered with flame-sprayed copper for heat conduction, a thin stainless steel coating for protection against corrosion, and a 2-in.-thick layer of asbestos insulation. The reaction section, prior to being insulated, is shown in Fig. 2.

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Fig. 1. Schematic Diagram of BrF₅ Fluorination Facility

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Fig. 2. Reaction Section of Reactor before
Installation of Asbestos Insulation

the scrub tower at the side near the top and are scrubbed by a concurrent spray of 1 to 2N KOH caustic solution containing 0.05N KI to promote re-action. A pump forces the scrub solution through either of two filters, where precipitated uranium compounds are collected, thus providing a measure of the uranium that passes through the NaF traps. The inert gases are vented through another scrubbing system for ventilation air.

B. Instrumentation

Throughout the equipment, temperatures are monitored with Chromel-Alumel thermocouples. The most important temperatures are recorded on three multipoint strip-chart instruments, and the other temperatures are monitored on a manually operated temperature indicator.

3. Filter and Disengaging Section of Reactor

The heated 11-in.-diam filter and disengaging section contains four 3-by 18-in. bayonet type sintered-metal filters. Two are 10- μ pore-diameter Monel; the other two are 5- μ pore-diameter nickel. To remove accumulated fines from the filters, each filter is automatically blown back with 0.14 std cu ft of nitrogen (supplied at 80 psig) in a 1.5-sec pulse every 24 min. The pulses are timed so that every 6 min one of the filters is blown back. The system is operated by solenoid valves (0.125-in. orifices) mounted within 6 in. of the outlet of the filters.

4. Sodium Fluoride Traps

Five in-series traps containing 1/8-in. sodium fluoride pellets are used for sorption of UF_6 from the off-gas. The first two traps each have a 12-kg NaF capacity and are heated by band heaters. The last three traps each have a 5-kg NaF capacity and are heated by asbestos-coated Nichrome wire.

5. Scrubber System

The off-gases, after passing through the NaF traps, are routed to the caustic scrubber system. Gases enter

Proportioning-type temperature controllers, operated by signals from the thermocouples, regulate electric power to the heaters of the four zones of the reactor section, the filter section, and the NaF traps. Controllers are also used to operate solenoid valves, which admit water to each of the four cooling zones on the reaction section.

The following pressures, differential pressures (ΔP), and gas flow-rates are measured by pneumatic transmitters and recorded on 4-in. strip-chart recorders or circular-chart recorders:

- (1) Total reactor ΔP .
- (2) Filter ΔP .
- (3) Disengaging section pressure.
- (4) Lower reaction section ΔP .
- (5) Middle reaction section ΔP .
- (6) Top reaction section ΔP .
- (7) Inlet-gas pressure.
- (8) Fluorine-feed-tank pressure.
- (9) Fluorine flow.
- (10) Oxygen flow.
- (11) Nitrogen flow.
- (12) BrF_5 -feed-tank pressure.

Flowrates of the oxygen, nitrogen, and fluorine, which are measured by pneumatic ΔP transmitters with integral orifices, are controlled by pneumatic valves. Flowrates of the BrF_5 and purges are measured by rotameters and are controlled manually.

Methods were tested for continuous in-line analysis and monitoring of the process-gas streams for process control and for determining the end point of reactions.

During the oxidation of UO_2 , oxygen is consumed in the reaction, resulting in a proportional decrease of oxygen concentration in the off-gas. In the fluorination of U_3O_8 with BrF_5 , oxygen is evolved as indicated in the reaction

The progress of these reactions was monitored by measuring the oxygen concentration in the off-gas using a Hays Oxygen Analyzer.

The operation of the Hays Oxygen Analyzer is based on the unique paramagnetism exhibited by oxygen and the temperature dependence of the paramagnetism. The analyzer consists of a measuring cell, a power supply, and a millivolt recorder. (Figure 3 is a schematic diagram of the oxygen-analyzing system.)

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Fig. 3. Schematic Diagram of Sample System for Hays Oxygen Analyzer

During the oxidation step, part of the off-gas evolved passes through a filter to remove particulate, and through a rotameter to measure the volume of gas sample flowing through the Hays Oxygen Analyzer. During the BrF_5 fluorination step, part of the off-gas evolved is routed through a trapping system to remove corrosive vapors such as UF_6 , BrF_5 , and bromine.

In the reaction of BrF_5 with U_3O_8 , bromine is one of the reaction products formed. Since bromine vapor is yellowish and known to absorb light at a wavelength of $546\text{ m}\mu$, the $\text{U}_3\text{O}_8 + \text{BrF}_5$ reaction was monitored by continuously measuring the bromine in the off-gas, using a DuPont photometric analyzer. Spectrophotometric measurements carried out by Steunenberg⁶ have revealed that BrF_5 , BrF_3 , and UF_6 do not interfere with bromine significantly in the $546\text{-m}\mu$ wavelength region.

The photometric analyzer system consisted of a flow-through cell with sapphire windows, a light source, filter sets, photocells and logarithmic amplifiers, a power supply, a control station, and a millivolt recorder. The analyzer was piped in series with the main off-gas stream, and provisions for heating the measuring cell were incorporated to avoid condensation of UF_6 , BrF_5 , or bromine in the cell.

An auxiliary calibration system was used to measure the partial pressure of bromine and nitrogen. After a gas sample was drawn into a previously evacuated flask, the total pressure of the mixture containing nitrogen and bromine was measured using a vacuum mercury manometer. The partial pressure of bromine and nitrogen was then determined by isolating the sample flask, absorbing the bromine fraction in a small amount of KOH solution, and measuring the fall in mercury level in the manometer.

The vapor pressure and volume correction for the amount of KOH solution added were also taken into consideration.

C. Reagents

Fluorine:	Supplied in 6-lb cylinders, 98.5% minimum purity, by General Chemical Division, Allied Chemical Co.
Oxygen:	Supplied by Liquid Carbonic Corp., in 220-cu ft cylinders, 99.5% minimum purity.
Nitrogen:	Supplied by Air Products Corp., vaporized from liquid form.
BrF ₅ :	Supplied by General Chemical Division, Allied Chemical Co., in 25-lb cylinders, 98% minimum purity. The BrF ₅ feed gas was analyzed for bromine-to-fluorine ratio during the runs, as described in Appendix C.
Alumina for fluid beds:	Supplied by Aluminum Co. of America, Type T-61 sintered alumina (sieve analyses given in Appendix D).
NaF:	Supplied by Harshaw Chemical Co., 1/8-in. pellets made by desorbing HF from pelletized sodium bifluoride.
UO ₂ :	Supplied by Nuclear Materials and Equipment Corp. Depleted UO ₂ and normal UO ₂ ; 1/2-in.-diam by 1/2-in.-long pellets, crushed into fragments. (Sieve analysis is given in Appendix D; sieve fractions of a representative sample are shown in Fig. 4.)
Fission products:	Added in the amounts shown in Table II.

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Fig. 4. Sieve Fractions of a Representative Sample of Fragmented UO_2 Pellets (see Appendix D for quantitative data)

TABLE II. Fission-product Compounds Added

Compound	Amount, g	
	With 2.2-kg UO ₂ Charge	With 4.4-kg UO ₂ Charge
SeO ₂	0.27	0.54
SrF ₂	11.70	23.41
RbF	8.87	17.74
Y ₂ O ₃	5.10	10.19
ZrO ₂	37.28	71.55
MoO ₃	39.87	79.74
RuO ₂	14.16	28.31
RhO	2.95	5.89
PdO	2.16	4.33
Ag ₂ O	0.03	0.059
CdO	0.07	0.146
In ₂ O	0.01	0.021
SnO ₂	0.11	0.21
Sb ₂ O ₅	0.04	0.089
I	1.43	2.86
CsF	18.92	37.85
BaO	10.80	21.59
La ₂ O ₃	9.10	18.21
CeO ₂	22.95	45.90
PrO ₂	10.87	21.74
Nd ₂ O ₃	33.06	66.13
Sm ₂ O ₃	6.16	12.31
Eu ₂ O ₃	0.23	0.46
Gd ₂ O ₃	0.09	0.18
	236.23	472.46

D. Operating Procedures

1. Bed Preparation

Before each run of the factorial experiments, the support-bed material and the fluid-bed material were weighed. For each run, the weight of alumina was chosen to give 40 w/o U₃O₈ in the reactor bed at the end of the oxidation step.

2. Prefluorination

Equipment and reactor beds were prefluorinated with fluorine at 550°C for 2 hr to form a protective layer of nickel fluoride on the equipment and to simulate bed material which had been used in a previous plutonium-recovery process cycle.

3. Fuel and Fission-product Charging

For each run, the specified charge of fragmented normal and depleted UO_2 pellets and powdered fission-product compounds was added to form a fluidized-packed bed at the base of the reactor. After prefluorination of the system, charging was done through the top flange (charging port).

4. Oxygen Step

For the 2.2-kg UO_2 charges, the UO_2 was oxidized to U_3O_8 by reaction at 450°C with 19.2 v/o oxygen for 6 hr in nitrogen. For the 4.4-kg UO_2 charges, the UO_2 was oxidized for 11 hr. Superficial velocity was 1.4 ft/sec. This step pulverized the fragmented pellets and provided a more reactive uranium oxide for the fluorination step with BrF_5 .

5. BrF_5 Step

The U_3O_8 was converted to UF_6 using BrF_5 . The conditions used varied according to the factorial experiment (discussed in Section III). BrF_5 was fed at ~19.7 or 11.3 v/o into the reaction section, which had been heated to 225 or 300°C . No external heat was supplied to the reactor during fluorination, and the reactor was cooled by the air-water system. Length of fluorination was mainly decided on the basis of bed-sample color, and feeding of the reactant was stopped when the bed lost its characteristic brown or black (UO_2F_2 - U_3O_8) color. The UF_6 produced was sorbed in the NaF traps, and the remainder of the off-gas was scrubbed in the caustic scrubber.

6. Sampling

a. Bed Samples. Samples of the fluid-bed material were extracted through the sample ports 18 and 36 in. above the bottom of the reaction section. The lower port was used for the shallower fluid-bed runs (2.2-kg UO_2 charge), and the upper port was used for the deeper bed runs (4.4-kg UO_2 charge). Before each ~20-g sample was taken, a small amount of material (20-60 g) was extracted to flush any entrapped material out of the lines. The flush material taken during the oxidation step was returned to the bed before the BrF_5 step. Flush material taken during the BrF_5 step was combined, and its uranium content determined for material-balance purposes. Bed samples taken during the oxygen step were ground to -200 mesh and submitted for uranium analyses; in some cases, the $^{235}\text{U}/^{238}\text{U}$ ratio was also determined. Bed samples taken during the BrF_5 step were also ground and analyzed for uranium.

b. Final Beds. After each run, the reactor bottom was opened and the free-flowing material was drained out. (The free-flowing material

was screened to separate the +8 mesh support bed from the fluid-bed portion.) Then the reactor was tapped to dislodge any accumulated fines from the filters or reactor walls. The fluid-bed portion and the tapped portion were separately reduced to a convenient sample size using a

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Fig. 5. Operator Withdrawing Off-gas Sample

riffle; the sample was then ground and submitted for uranium analysis. The support bed was leached with ~50 v/o HNO_3 , dried, and sampled. Both the leach liquor and the solid portions were subsequently analyzed for uranium. Error analysis for bed samples is described in Appendix E.

c. Gas Samples. During the BrF_5 step, both the inlet and off-gas streams were periodically sampled. Samples were drawn into 6-in.-diam Monel spheres which had been evacuated and heated to about 100°C (as shown in Fig. 5). The material collected was transferred into Kel-F tubes and hydrolyzed in a 1% aqueous solution of hydrazine. About 10 ml of concentrated HNO_3 was added after hydrolysis to dissolve

a flocculent yellow precipitate that formed. Hydrolysis solutions were analyzed for bromine, fluorine, and uranium content.

d. NaF Traps. After the BrF_5 step, the sodium fluoride traps were purged overnight or longer with nitrogen to remove sorbed bromine. (However, even after extended periods of purging, the bromine odor and color could be detected when the traps were discharged.) The NaF was then ground in a disc mill, riffled to a convenient sample size, and submitted for uranium analysis.

e. Scrubber. After each run, the scrubber solution was sampled and tested for basicity.

The filter chambers were drained of caustic. The filter pads were then leached with a hot 50% HNO_3 solution to dissolve the filtered uranium precipitate, and the solution was submitted for uranium analysis.

The general procedure for making a run consists of prefluorinating the alumina fluidized bed and the alumina support bed, charging the fragmented uranium oxide pellets and powdered fission-product compounds to the fluid-bed reactor, oxidizing the UO_2 fragments to U_3O_8 fines, and fluorinating the oxide fines with BrF_5 to produce volatile UF_6 . The UF_6 is collected in beds of NaF pellets. Off-gas samples and bed samples are taken periodically throughout the fluorination step to determine the reaction rate and BrF_5 utilization efficiency.

III. OPERATING CONDITIONS

A fractional factorial experiment^{7,8} was used to determine the effects of the process variables on the results obtained from the oxidation step and BrF_5 step using a minimum number of runs. Six independent (controlled) variables were thought to have possible beneficial or detrimental effects on the UF_6 production rate and on the utilization efficiency of the BrF_5 : (1) fluid-bed temperature (225 and 300°C), (2) BrF_5 partial pressure (~0.16 and ~0.29 atm, i.e., ~12 or ~20 v/o), (3) superficial gas velocity (~0.54 and ~0.89 ft/sec), (4) quantity of UO_2 charge (2.2 and 4.4 kg), (5) particle size of the alumina-bed material (-100 mesh and 48-100 mesh), and (6) the presence and absence of inactive fission-product compounds in the bed. Other independent variables, such as (1) the ratio of UO_2 to inert alumina, (2) conditions for the oxidation of UO_2 to U_3O_8 , (3) the quality of the reagents, and (4) equipment and operating procedures, were held constant.

Table III shows the design of the fractional factorial experiment for the BrF_5 fluorination. Table IV shows the operating conditions for the prefluorination, oxidation, and fluorination steps, including the actual high (+) and low (-) values of the variables in the fluorination step. Runs 3 and 4 were duplicate runs whose results were compared for error analysis.

As shown in Table III, there are seven sources of variation (columns) in an eight-run factorial experiment. The seventh variable column was designated for estimation of the experimental error, it being assumed that the effects of interactions of the other variables are unimportant. This is usually a good assumption in physical situations where the high and low levels of the variables are not widely different. Actually, the effects of all variables were influenced by first- and higher-order interactions in this

TABLE III. Design of Fractional Factorial Experiment for BrF_5 Fluorination of U_3O_8

+ designates the high level of the variable
- designates the low level of the variable

Run	Bed Temperature	BrF_5 Partial Pressure	Superficial Gas Velocity	UO_2 Charge	Alumina Particle Size	Fission Products	Error	Result
4	+	+	-	+	-	-	-	Y_4
6	+	+	+	-	-	+	+	Y_6
8	+	-	+	+	+	+	-	Y_8
11	+	-	-	-	+	-	+	Y_{11}
5	-	-	-	+	-	+	+	Y_5
7B	-	+	-	-	+	+	-	Y_{7B}
9	-	+	+	+	+	-	+	Y_9
10	-	-	+	-	-	-	-	Y_{10}

TABLE IV. Operating Conditions for Prefluorination, Oxidation, and Fluorination Steps

Run	Independent Variable							Inlet Pressure, psig
	Fluid-bed Temperature, ^a °C	Inlet Partial Pressure in Nitrogen, atm	Superficial Velocity of Fluidizing Gas, ^b ft/sec	UO ₂ Charge, kg	Alumina Particle Size, ^c mesh	Fission Products ^d	Time, hr	
Prefluorination Step (Fluorine)								
All runs	550	~0.064	1.5	None	See BrF ₅ step	Absent	2:0	3 to 5
Oxidation Step (Oxygen)								
All runs	450	~0.270	1.4	See BrF ₅ step	See BrF ₅ step	See BrF ₅ step	6.0 or 11.0 ^e	5 to 7
Fluorination Step (BrF ₅) ^b								
3	300	0.291	0.54	4.4	-100	Absent	3.0	6.0
4	300	0.284	0.53	4.4	-100	Absent	3.0	6.0
5	225	0.155	0.54	4.4	-100	Present	6.0	5.5
6	300	0.291	0.93	2.2	-100	Present	2.0	7.0
7A	225-465	0.261	0.56	2.2	48-100	Present	3.0	4.5
7B	225	0.260	0.54	2.2	48-100	Present	3.0	5.0
8	300	0.180	0.94	4.4	48-100	Present	4.0	10.0
9	225	0.322	0.80	4.4	48-100	Absent	3.0	11.0
10	225	0.163	0.90	2.2	-100	Absent	3.0	7.0
11	300	0.153	0.59	2.2	48-100	Absent	3.0	4.0

^aThe temperature of the filter zone was maintained at 250°C for all processing steps.

^bIn some runs, the desired values for BrF₅ partial pressure or superficial gas velocity were not attained. For these runs, the results (UF₆ production rate, diminishing-sphere rate constant, and BrF₅ utilization efficiency) were appropriately adjusted (i.e., linearly smoothed).

^cA 2.0-kg support bed of -1/4, +8 mesh Type T-61 Alcoa alumina was used in all runs. A quantity of fluidized alumina, Alcoa Type T-61, was used that would give a bed containing 40 w/o U₃O₈ at the end of the oxidation step.

^dThe relative quantities of fission-product compounds represent the amounts that would be present in five charges of UO₂.

^eThe oxidation step was 6.0 hr for 2.2 kg of UO₂ and 11.0 hr for 4.4 kg of UO₂.

fractional factorial experiment. In general, interactions must be assumed to be unimportant since interaction effects are not computable in highly fractionated experiments such as this one.

Calculation of an effect of a variable involves subtracting the average result for runs in which the variable was at its low level from the average result for runs where the variable was at its high level. This is shown in Table V. Comparison of Tables III and V reveals that in a calculation the effects of the other independent variables cancel out; thus, for example, Eq. 1 in Table V is used to calculate the effect of temperature, independent of the effects of all other variables (if interaction effects are not present).

TABLE V. Determination of Effects of Independent Variables for BrF₅ Fluorination of U₃O₈

Fluid-bed temperature: $E_T = \frac{(Y_4 + Y_6 + Y_8 + Y_{11}) - (Y_5 + Y_{7B} + Y_9 + Y_{10})}{4}$	(1)
Partial pressure of BrF ₅ : $E_{p.p.} = \frac{(Y_4 + Y_6 + Y_{7B} + Y_9) - (Y_5 + Y_8 + Y_{10} + Y_{11})}{4}$	(2)
Superficial gas velocity: $E_{Vel} = \frac{(Y_6 + Y_8 + Y_9 + Y_{10}) - (Y_4 + Y_5 + Y_{7B} + Y_{11})}{4}$	(3)
Weight of charge of UO ₂ : $E_{Chg} = \frac{(Y_4 + Y_5 + Y_8 + Y_9) - (Y_6 + Y_{7B} + Y_{10} + Y_{11})}{4}$	(4)
Alumina particle size: $E_d = \frac{(Y_{7B} + Y_8 + Y_9 + Y_{11}) - (Y_4 + Y_5 + Y_6 + Y_{10})}{4}$	(5)
Presence of fission products: $E_{f.p.} = \frac{(Y_5 + Y_6 + Y_{7B} + Y_8) - (Y_4 + Y_9 + Y_{10} + Y_{11})}{4}$	(6)
Error: $E_{Error} = \frac{(Y_5 + Y_6 + Y_9 + Y_{11}) - (Y_4 + Y_8 + Y_{7B} + Y_{10})}{4}$	(7)

The overall result of an experiment at any condition within the range of those studied can be estimated by the following linear-interpolation formula, which assumes that all effects are linear over the range studied:

$$Y = \bar{Y} + \frac{E_T}{2} (\phi_T) + \frac{E_{P.P.}}{2} (\phi_{P.P.}) + \frac{E_{Vel}}{2} (\phi_{Vel}) + \frac{E_{Chg}}{2} (\phi_{Chg}) + \frac{E_d}{2} (\phi_d) + \frac{E_{F.P.}}{2} (\phi_{F.P.}) + e, \quad (1)$$

where $\bar{Y}$ is the average result at $\phi_T = \phi_{P.P.} = \phi_{Vel} = \phi_{Chg} = \phi_d = \phi_{F.P.} = 0$, and e is the experimental error, a random variable with zero mean and the experimental standard deviation. The ϕ variables are defined by

$$\phi_i = \frac{\text{Desired value of } i - \frac{i_{(+)} + i_{(-)}}{2}}{\frac{i_{(+)} - i_{(-)}}{2}}, \quad (2)$$

or, for the specific example of temperature,

$$\phi_T = \frac{T - \frac{T_{(+)} + T_{(-)}}{2}}{\frac{T_{(+)} - T_{(-)}}{2}} = \frac{T - 535.5}{37.5},$$

with T in $^{\circ}\text{K}$.

The effect of temperature on reaction rate is usually exponential and the effect of BrF_5 partial pressure as well as the effects of other variables may not be linear, but for practical engineering purposes, a linear interpolation may be warranted over the ranges used in this study.

The results (Y_i) measured in the BrF_5 step were the UF_6 production rate, diminishing-sphere rate constant, and BrF_5 utilization efficiency.

The experimental error can be calculated from E_{Error} in combination with the results of the two repeated runs (Runs 3 and 4). The variance of an effect is then given by

$$V_{\text{eff}} = \frac{(E_{\text{Error}})^2 + \frac{1}{2}(Y_3 - Y_4)^2}{2}, \quad (3)$$

and the standard error for effects is

$$SE_{\text{eff}} = \sqrt{V_{\text{eff}}} \quad (4)$$

Note: The variance of a result (Y_i) is twice the variance of an effect (E_i).

If there is good reason to believe that one or more of the six independent variables have no effect on the result, the effects calculated for these variables can be used to improve the estimate of the experimental error. Thus, in general, the variance of an effect is

$$V_{\text{eff}} = \frac{\sum_1^n E_{\text{Error}}^2 + \sum_1^m \frac{1}{2}(Y_a - Y_b)^2}{n + m} \quad (5)$$

The second sum in the numerator provides for the possibility that more than one run is repeated. The statistical significance of the measured effects can be determined by using a t test for each effect (E_i),

$$t_i = \frac{E_i}{SE_{\text{eff}}} \quad (6)$$

using $n + m$ degrees of freedom in a t table. For example, if an effect were 5 lb/hr and the standard error were 2 lb/hr determined with nine degrees of freedom, $t = 2.5$. The t table shows that there is less than one chance in 20 that the calculated effect, 5 lb/hr, was due to experimental error.

As shown in Table VI, the design of the fractional factorial experiment for the BrF_5 step allowed investigation of the effects of three of the

TABLE VI. Design of Factorial Experiment for Oxidation of UO_2
Using 19.2 v/o O_2 , 1.4-ft/sec gas velocity, 450°C,
3-in.-diam fluid-bed reactor

Run	A, Alumina Particle Size	B, UO_2 Charge	C, Fission Products	AB Error	AC Error	BC Error	ABC Error	Result
10	-	-	-	+	+	+	-	Y_{10}
11	+	-	-	-	-	+	+	Y_{11}
4	-	+	-	-	+	-	+	Y_4
9	+	+	-	+	-	-	-	Y_9
6	-	-	+	+	-	-	+	Y_6
7B	+	-	+	-	+	-	-	Y_{7B}
5	-	+	+	-	-	+	-	Y_5
8	+	+	+	+	+	+	+	Y_8

Variable	Levels	
	Low (-)	High (+)
Alumina particle size	-100 mesh	48 to 100 mesh
UO_2 charge	2.2 kg	4.4 kg
F.P. (Fission products)	Absent	Present

independent variables (alumina particle size, UO_2 charge, and fission products) in the oxidation step also. Table VII shows the equations for calculating the effects. Equations 4-7 in Table VII can be used to estimate the experimental error (E_{Error}), assuming that no interactions are present. Measurements (Y_i) made during the oxidation step included the UO_2 reaction rate, the degree of homogeneity of the fluid bed, and the ratio of ^{235}U to ^{238}U , the last-mentioned data for evaluating a proposed accountability scheme for plutonium.

TABLE VII. Determination of Effects of Independent Variables for Oxidation of UO_2

$$E_A = E_d = \frac{(Y_{7B} + Y_8 + Y_9 + Y_{11}) - (Y_4 + Y_5 + Y_6 + Y_{10})}{4} \quad (1)$$

$$E_B = E_{\text{Chg}} = \frac{(Y_4 + Y_5 + Y_8 + Y_9) - (Y_6 + Y_{7B} + Y_{10} + Y_{11})}{4} \quad (2)$$

$$E_C = E_{\text{F.P.}} = \frac{(Y_5 + Y_6 + Y_{7B} + Y_8) - (Y_4 + Y_9 + Y_{10} + Y_{11})}{4} \quad (3)$$

$$E_{AB} = E_{\text{Error}} = \frac{(Y_6 + Y_8 + Y_9 + Y_{10}) - (Y_4 + Y_5 + Y_{7B} + Y_{11})}{4} \quad (4)$$

$$E_{AC} = E_{\text{Error}} = \frac{(Y_4 + Y_{7B} + Y_8 + Y_{10}) - (Y_5 + Y_6 + Y_9 + Y_{11})}{4} \quad (5)$$

$$E_{BC} = E_{\text{Error}} = \frac{(Y_5 + Y_8 + Y_{10} + Y_{11}) - (Y_4 + Y_6 + Y_{7B} + Y_9)}{4} \quad (6)$$

$$E_{ABC} = E_{\text{Error}} = \frac{(Y_4 + Y_6 + Y_8 + Y_{11}) - (Y_5 + Y_{7B} + Y_9 + Y_{10})}{4} \quad (7)$$

Examples of calculations of experimental error are given in Section 6 of Appendix F.

IV. RESULTS AND DISCUSSION

A. Oxidation of UO_2 1. Rate of Oxidation of UO_2

Table VIII lists average oxidation rates, together with the effects of using high (+) levels of the variables, alumina particle size, UO_2 charge, and fission products. The standard error of the effects was estimated to be 1.0 lb/hr. Therefore, any of the observed effects might have been caused by experimental error. However, the effects agree with physical intuition regarding sign and relative magnitude. That is, the larger charge gave a larger average reaction rate because more surface area was available for reaction; the larger particle size of alumina gave lower reaction rates, probably due to poorer fluidization characteristics, and the effect of the presence or absence of inactive fission-product compounds is negligibly small, as expected.

TABLE VIII. Rate of Oxidation of UO_2 ; Effects of Using High Levels of Independent Variables on Oxidation Rate

Run	Average Oxidation Rate to $F = 0.5$, lb/hr	Variable	Effect, lb/hr ^a
3	5.0	A Alumina particle size	
4	5.9	of 48 to 100 mesh	-1.47
5	9.1	B 4.4-kg UO_2 charge	1.73
6	4.6	C Presence of fission	
7A	2.9	products	-0.38
7B	3.6	AB	-0.78
8	4.2	AC	-1.49
9	6.4	BC	0.85
10	5.5	ABC	-1.19
11	5.1		

^aMultiply by 19.49 to get lb/(hr)(ft²).

The utilization of oxygen was calculated to be as high as 10% during early portions of the runs.

2. Particle Size of U_3O_8

The particle-size distribution of the U_3O_8 fines produced by the oxidation of UO_2 in four runs was measured, using a Coulter counter. The results showed that the diameter of most of the U_3O_8 particles is in the range 0.3-5 microns and that the average particle diameter is about 3 microns. This result agrees with work by Wilson and Tomlinson at ORNL.⁹

3. Homogeneity of the Fluid Bed

For oxidation of UO_2 , fragmented pellets are poured into the alumina bed. Because of their high density, the UO_2 pellets sink to the bottom of the reactor when the alumina is fluidized, forming a fluidized-packed-bed section. During oxidation, transfer of the pulverized U_3O_8 fines to the freely fluidized section of the bed is expected, and the distribution of U_3O_8 fines in the reactor bed may not be uniform because of elutriation, segregation, and/or agglomeration of fines.

To determine the distribution of U_3O_8 in the fluidized bed, a homogeneity factor (U_R , the amount of uranium in the reactor/ U_B , the amount of uranium in the fluid bed, as determined by analysis of bed samples) has been defined and the influence on this factor of (1) changing the UO_2 charge size, (2) changing the alumina particle size, and (3) adding fission products to the fluidized bed has been measured. Table IX gives the calculated effects of these three independent variables on the homogeneity factor. Since effects of interactions are not common in many physical

TABLE IX. Effects of Three Independent Variables on Homogeneity Factor for Oxidation Step

Run	Homogeneity Factor, $U_R/U_B = (\text{Total U in reactor})/(\text{U in bed by analysis})$
3 (Duplicate of Run 4)	1.138
4	1.245
5	1.116
6	1.127
7A (Duplicate of Run 7B)	2.133
7B	2.088
8	2.120
9	2.687
10	1.341
11	2.619

Effects of Variables on U_R/U_B

Variable	Effect
A (Particle size)	$E_d = 1.171$
B (Charge)	$E_{\text{Chg}} = -0.001$
C (Fission product)	$E_{\text{F.P.}} = 0.360$
AB = Error	$E_{AB} = 0.051$
AC = Error	$E_{AC} = -0.188$
BC = Error	$E_{BC} = 0.012$
ABC = Error	$E_{ABC} = 0.030$

Using four error effects, duplicate Runs 3 and 4, and duplicate Runs 7A and 7B gives $V_{\text{eff}} = 0.0076$ and $SE_{\text{eff}} = \sqrt{V_{\text{eff}}} = 0.0873$

t Test (Six degrees of freedom)

$t_d = \frac{E_d}{SE} = 13.413$	Significant at 99%
$t_{\text{Chg}} = \frac{E_{\text{Chg}}}{SE} = 0.011$	Not significant
$t_{\text{F.P.}} = \frac{E_{\text{F.P.}}}{SE} = 4.124$	Significant at 99%

situations, the effects of the interaction variables were used to estimate the experimental error. The variance, $V_{\text{eff}} = \frac{1}{2}(Y_a + Y_b)/2$, between the duplicate Runs 3 and 4 and duplicate Runs 7A and 7B were combined into the variance calculated from the effects of the dummy variables to improve the estimate of the experimental error.

An analysis of the variance shows that the effects of alumina particle size and the presence of fission products are significant at the 99% level. The effect of charge size was insignificant.

Using an alumina particle size of -100 mesh rather than 48 to 100 mesh decreases the homogeneity factor by 1.171. This means that the

U_3O_8 fines are more uniformly mixed in the -100 mesh alumina bed. The more uniform distribution of U_3O_8 in the finer alumina bed after 2 hr of oxidation is shown in Fig. 6. The uranium concentration remained relatively constant after a few hours and represented less than the total amount charged to the reactor.

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Fig. 6. Uranium Content of Bed Samples during Oxidation Step

The addition of fission products reduced the homogeneity factor by 0.360, making the distribution of uranium in the bed more homogeneous. Since the fission products were added to the bed in the form of fine powders, this influence is ascribed to reducing the average size of particles of the fluidized bed.

The absence of any effect of the size of the UO_2 charge may indicate that there is no effect of the depth of the fluidized bed or the port from which the grab samples were withdrawn. The uranium-to-alumina ratio was held constant (40 w/o U_3O_8), and therefore larger charges of UO_2 were associated with deeper beds of alumina. The deep-bed runs were sampled through a port 36 in. from the bottom of the reactor, and the shallow-bed runs were sampled from a port 18 in. from the bottom.

4. Evaluation of a Method of Determining Plutonium Content for Accountability Purposes

For accountability purposes, the plutonium content of spent fuels must be known, and a method for plutonium analysis is being considered that is based on measuring the weight of input $\text{UO}_2\text{-PuO}_2$ and the uranium-to-plutonium ratio in bed samples. In this method, only the

uranium and plutonium need be homogeneously mixed; homogeneity need not be obtained with respect to other constituents of the bed such as alumina. To evaluate this method, ^{235}U was used as a stand-in for plutonium in this series of tests. Pellets having two different ^{235}U contents were introduced; 10% of the pellets contained depleted uranium (0.221% ^{235}U), and 90% contained normal uranium (0.730% ^{235}U). The ratio $^{235}\text{U}/^{238}\text{U}$ was determined from periodic bed samples taken during oxidation step. These ratios have been plotted as a function of time in Fig. 7 where they are compared with the theoretical ^{235}U content. Table X gives the effects of the variables, calculated using the $^{235}\text{U}/^{238}\text{U}$ ratio in the final grab sample of the oxidation step as the dependent variable.

The analysis of the variance indicated that none of the independent variables affect the isotopic ratio. Table X indicates that the difference between the mean of the experimental values and the theoretical mean is similar to the standard error. Since the standard error is low, it has been concluded that if plutonium behavior is the same as that of ^{235}U , the plutonium input to the fluid-bed reactor can be obtained to at least $\pm 2.00\%$ from (1) the Pu/U ratio for the final grab sample of the oxidation step and (2) the input weight of $\text{UO}_2\text{-PuO}_2$.

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Fig. 7. $^{235}\text{U}/^{238}\text{U}$ Ratio for Oxidation Step

B. BrF_5 Fluorination of U_3O_8

1. General Operating Characteristics

In general, the operation of the reactor was smooth, and all equipment operated satisfactorily throughout the fluorination step. In all cases, the beds were well fluidized and free-flowing at the end of the processing cycle. Temperature control was, in general, within $\pm 5^\circ\text{C}$ of the desired temperature. In some runs in which the charges contained fission products, small (3/8-in.) agglomerates were found in the alumina beds. Their formation was related to the presence of Ba, Cs, Mo, and Rb. Presence of the agglomerates did not affect the operation during the runs or hinder removal of the beds at the end of the run.

TABLE X. $^{235}\text{U}/^{238}\text{U}$ Ratio in Final Grab Sample for Oxidation Step

Run	$^{235}\text{U}/^{238}\text{U}$ Ratio of Final Bed Sample
3 (Duplicate of Run 4)	6.73×10^{-3}
4	6.76×10^{-3}
5	6.77×10^{-3}
6	6.78×10^{-3}
7A (Duplicate of Run 7B)	6.75×10^{-3}
7B	6.83×10^{-3}
8	6.92×10^{-3}
9	6.78×10^{-3}
10	6.74×10^{-3}
11	6.59×10^{-3}
Average 6.77×10^{-3}	

Theoretical average for a homogeneous mixture = 6.79×10^{-3}

Effects on $^{235}\text{U}/^{238}\text{U}$ of Using (+) Level of Variable

Variable	Effect
A (Particle size)	$E_d = 0.0175 \times 10^{-3}$
B (Charge)	$E_{\text{Chg}} = 0.0725 \times 10^{-3}$
C (Fission products)	$E_{\text{F.P.}} = 0.1075 \times 10^{-3}$
AB (Error)	$E_{AB} = 0.0675 \times 10^{-3}$
AC (Error)	$E_{AC} = 0.0825 \times 10^{-3}$
BC (Error)	$E_{BC} = -0.0325 \times 10^{-3}$
ABC (Error)	$E_{ABC} = -0.0175 \times 10^{-3}$

Using four dummy variables, duplicate Runs 7A and 7B, and duplicate Runs 3 and 4 gives $V_{\text{eff}} = 27.3 \times 10^{-10}$, and $SE_{\text{eff}} = \sqrt{V_{\text{eff}}} = 5.28 \times 10^{-5}$

t Test (Six degrees of freedom)

$$\left. \begin{aligned} t_d &= \frac{E_d}{SE} = 0.334 \\ t_{\text{Chg}} &= \frac{E_{\text{Chg}}}{SE} = 1.375 \\ t_{\text{F.P.}} &= \frac{E_{\text{F.P.}}}{SE} = 2.036 \end{aligned} \right\} \text{All not significant, 95\% test}$$

In Run 7A, in the initial attempt to complete the BrF_5 fluorination, a malfunction of the reactor cooling system allowed a temperature excursion to occur near the bottom of the fluidized portion of the bed. The temperature reached a maximum of 465°C about 12 min after the introduction of BrF_5 and remained above 400°C for about 10 min; between 300 and 400°C for about 20 min; and between the set point, 225°C , and 300°C for about 30 min. The temperature excursion did not produce any operational problems, but, because of the poor temperature control, the results of the run were not compared to results of other runs.

In Run 7B, made with a working cooling system, a temperature excursion was observed at the bottom of the fluidized bed, but was limited to a maximum temperature of 270°C ; the temperature was above the set

point of 225°C for only 10 min. For the remainder of the 3-hr BrF_5 fluorination, the temperature of the entire fluidized bed was $225 \pm 5^\circ\text{C}$. The temperature control in Run 7B was satisfactory for comparison with the other runs in the series. Since there was a tendency for temperature excursions in this run, the combination of conditions used (see Table IV) is not recommended for process application.

2. UF_6 Production Rate

Table XI presents average UF_6 production rates for nine runs, up to times at which the fraction F of the original uranium charge converted to UF_6 was 0.50, 0.667, and 0.75.* The results called "Average Total UF_6 Production Rates in Entire System" were obtained by analysis of the gas stream leaving the reactor; the results called "Average Fluid-bed UF_6 Production Rates" were obtained by analyzing bed samples; the

TABLE XI. UF_6 Production Rates^a

Run	To $F^b = 0.50$	To $F^b = 0.667$	To $F^b = 0.75$
<u>Average Total UF_6 Production Rate in Entire System, lb/hr^c</u>			
3	6.1	6.1	6.0
4	7.5	7.4	7.0
5	3.7	3.8	3.8
6	8.0	8.2	7.7
7B	4.1	4.2	4.1
8	6.2	5.0	4.2
9	8.8	9.0	8.6
10	3.9	4.0	3.7
11	3.7	3.9	3.7
<u>Average Fluid-bed UF_6 Production Rate, lb/hr^c</u>			
3	9.9	7.6	6.8
4	8.6	7.4	6.7
5	3.6	4.3	3.9
6	8.1	8.4	7.7
7B	2.9	3.0	3.1
8	4.7	3.2	2.4
9	6.9	7.3	7.1
10	2.8	3.1	2.8
11	3.3	3.4	3.1
<u>Average "Elsewhere" UF_6 Production Rate, lb/hr^c</u>			
3	-3.8	-1.5	-0.81
4	-1.1	0.02	0.36
5	0.15	-0.40	-0.16
6	-0.11	-0.18	-0.09
7B	1.16	1.20	1.02
8	1.52	1.84	1.82
9	1.84	1.67	1.45
10	1.10	0.97	0.88
11	0.45	0.44	0.54

^aCorrected to rates for average partial pressure and gas velocity.

^bFraction of original uranium converted to UF_6 .

^cMultiply by 19.49 to get lb/(hr)(ft²).

*Examples of sample calculations are detailed in Section 1 of Appendix F.

differences between these are called the "Average 'Elsewhere' UF_6 Production Rates." The assumption is that, although most of the reaction between U_3O_8 and BrF_5 occurs in the fluidized bed, part of the U_3O_8 (probably in the form of fines) is deposited on the filters or the disengaging chamber surfaces, or is otherwise segregated from the fluidized bed, and also reacts with BrF_5 . The effects of this reaction can be found from the off-gas analysis, but are not revealed by analysis of the bed samples. The fact that the difference is sometimes negative may indicate a constant bias between the two methods of determining UF_6 production rates caused, for example, by nonhomogeneous distribution of uranium in the alumina bed. However, of primary interest in discussing the "fluid-bed" and "elsewhere" rates are effects of the independent variables on these rates. Since these effects are differences in rates, a constant bias would not affect the calculated effects. The primary reason for dividing the Average Total UF_6 Production Rates into two individual rates is to obtain a more meaningful analysis of the effects of independent variables on the UF_6 production rates.

Table XII presents the effects computed as described in Table V. Appendix F shows that the standard error of an effect is of the order of 0.8. Therefore most of the effects in Table XII cannot be assumed to be statistically significant; i.e., they could well have resulted from experimental errors. Nevertheless, the results presented in Table XII are the best estimates of the effects available from the experimental data. In fact, the probable error associated with these effects is only half of what would have resulted from a one-variable-at-a-time sequence of the same number of runs.

TABLE XII. Effects of Independent Variables on UF_6 Production Rates

Fraction Reacted	Temperature	Partial Pressure of BrF_5	Superficial Gas Velocity	UO_2 Charge	Alumina Particle Size	Fission Products
<u>Effects on Total UF_6 Production Rate, lb/hr^a</u>						
0.50	1.24	2.7	1.95	1.63	-0.09	-0.50
0.667	0.85	3.0	1.72	1.24	-0.33	-0.74
0.75	0.59	3.0	1.40	1.10	-0.39	-0.81
<u>Effects on Fluid-bed UF_6 Production Rate, lb/hr^a</u>						
0.50	2.1	3.0	1.04	1.67	-1.31	-0.60
0.667	1.18	3.0	0.96	1.07	-1.52	-0.58
0.75	0.74	3.1	0.83	0.83	-1.35	-0.65
<u>Effects on "Elsewhere" UF_6 Production Rate, lb/hr^a</u>						
0.50	-0.86	-0.34	0.91	-0.04	1.22	0.10
0.667	-0.33	-0.04	0.76	0.17	1.19	-0.16
0.75	-0.14	-0.08	0.58	0.27	0.96	-0.16

^aMultiply by 19.49 to get lb/(hr)(ft²).

Consider the effect E_t of the temperature of the bed. Table XII shows that increasing the bed temperature from 225 to 300°C increases the rate of UF_6 production by approximately 1 lb/hr. Comparison of "fluid-bed" and "elsewhere" effects shows this increase occurred entirely in the bed, as expected, since only the bed temperature had been increased. The effect of increased bed temperature on "Reaction Elsewhere Rates" is apparently negative. Increasing the bed temperature increased the rate of reaction in the bed, which depleted the available BrF_5 before the gas stream reached the filter chamber, and thereby reduced the rate of reaction elsewhere. A similar effect was observed for BrF_5 concentration (i.e., BrF_5 partial pressure), the variable that produced the greatest effect on UF_6 production rate in the present work. In contrast, increasing the superficial gas velocity increased the production rates both in the bed and elsewhere; the increase in fluid-bed production rate presumably was due to the increased feed rate of BrF_5 , and the increase in production rate elsewhere may have been due to increased elutriation of fines. Increasing the amount of UO_2 pellets charged increased the UF_6 production rate in the bed, probably because of the increased quantity of U_3O_8 in the bed; as expected, no effect on the UF_6 production rate elsewhere is apparent. The effect of larger alumina particle diameter decreased the UF_6 production rate in the bed, presumably because of poorer fluidization quality. Since more BrF_5 was then available at other sites, the production rate elsewhere increased. The two effects cancelled each other, and no significant change was detected in the total production rate. The effect of adding fission products was small, as expected. Qualitatively, a temperature of 300°C, a BrF_5 inlet partial pressure of 0.29 atm, a superficial gas velocity of 0.89 ft/sec, and a UO_2 charge of 4.4 kg had positive effects on (that is, increased) the UF_6 production rate. These data are in good agreement with the data of Gabor and Ramaswami³ and Anastasia.⁴

The effect of the independent variables on uranium retention in the NaF traps is discussed in Appendix G, and uranium material balances are given in Appendix H.

3. Diminishing-sphere Rate Constants

The diminishing-sphere rate law is expected to apply to the BrF_5 fluorination of U_3O_8 since the products are gaseous Br_2 and UF_6 and the solid U_3O_8 is continuously consumed. Diminishing-sphere rate constants were computed for the U_3O_8 - BrF_5 reaction in the fluid bed by plotting $(1 - F)^{1/3}$ against time and using the slope of a fitted straight line. Table XIII shows the results, together with the effects of the independent variables on the rate constant. The standard error of an effect was estimated to be $2.2 \times 10^{-3} \text{ min}^{-1}$. The results show the expected increase in rate constant at higher temperature, higher partial pressure of BrF_5 , and greater superficial gas velocity. However, it is not clear why the alumina particle size did not affect the rate constant.

TABLE XIII. Diminishing-sphere Rate Constants for BrF_5 Fluorination of U_3O_8 :
Effects of Independent Variables on Rate Constant

Run	Rate Constant, k , min^{-1}	Variable	Effect, min^{-1}
3	10.7×10^{-3}	Temperature	3.6×10^{-3}
4	8.3×10^{-3}	Partial pressure of BrF_5 (inlet)	3.6×10^{-3}
5	4.1×10^{-3}	Superficial gas velocity	3.9×10^{-3}
6	17.2×10^{-3}	UO_2 charge	-1.9×10^{-3}
7B	8.6×10^{-3}	Alumina particle size	0.35×10^{-3}
8	10.6×10^{-3}	Fission products	1.66×10^{-3}
9	10.2×10^{-3}		
10	6.9×10^{-3}		
11	8.4×10^{-3}		

The data for the diminishing sphere rate constant are in good agreement with the data of Jarry and Steindler¹ and Anastasia.⁴

4. BrF_5 Utilization Efficiency

As with UF_6 production rates, BrF_5 utilization efficiency was separated into the results for reaction in the fluid bed, and the results for reaction elsewhere. The values are shown in Table XIV. Table XV presents

TABLE XIV. BrF_5 Utilization Efficiency^a

Run	To F ^b = 0.5	To F ^b = 0.667	To F ^b = 0.75
<u>Average Total BrF_5 Utilization Efficiency, %</u>			
3	94	85	80
4	78	71	68
5	50	51	51
6	63	61	58
7B	32	31	31
8	68	56	47
9	55	51	47
10	42	40	36
11	67	64	61
<u>Average Fluid-bed BrF_5 Utilization Efficiency, %</u>			
3	186	140	125
4	85	70	63
5	46	57	53
6	57	57	51
7B	21	20	21
8	49	36	28
9	37	36	35
10	24	25	23
11	44	45	42
<u>Average "Elsewhere" BrF_5 Utilization Efficiency, %</u>			
3	-92	-55	-45
4	-7.0	1.2	4.8
5	3.5	-6.2	-1.7
6	5.4	4.3	7.0
7B	10.6	10.7	9.8
8	18.5	20	18.5
9	18.7	14.8	12.6
10	18.2	14.9	13.6
11	23	18.8	19.3

^aCorrected to values for average partial pressure of BrF_5 and average gas velocity.

^bFraction of original uranium converted to UF_6 .

TABLE XV. Effects of Independent Variables on BrF_5 Utilization Efficiency

Fraction Reacted	Independent Variable					Fission Products
	Temperature	Partial Pressure of BrF ₅	Superficial Velocity	UO ₂ Charge	Alumina Particle Size	
<u>Effects on Total BrF₅ Utilization Efficiency, %</u>						
0.50	24	0.3	0.6	11.8	-2.9	-7.5
0.667	19.9	0.9	-2.5	8.4	-5.1	-6.9
0.75	17.1	2.2	-5.5	6.5	-6.9	-6.5
<u>Effects on Fluid-bed BrF₅ Utilization Efficiency, %</u>						
0.50	27	9.2	-7.0	17.6	-15.6	-3.8
0.667	17.4	5.0	-9.9	13.1	-17.7	-1.8
0.75	13.3	6.1	-10.4	10.4	-16.1	-2.4

the effects of the different variables on the total BrF_5 utilization efficiency and on the BrF_5 utilization efficiency in the fluid bed. Since the standard error of an effect was estimated to be approximately 8%, only the observed effect of temperature and the observed effect of UO_2 charge are thought to have been caused by other than experimental error. As for the standard error for the UF_6 production rates, the standard error is half of what would have been obtained from the results of the same number of runs in which one variable was changed in a run. The effects of an independent variable on BrF_5 utilization efficiency elsewhere may be obtained in Table XV from the difference between the total effect of an independent variable and its effect in the fluid bed. The general directions and magnitudes of the effects in Table XV agree with physical intuition. The effect of the higher temperature is to increase the BrF_5 utilization efficiency in the bed but not elsewhere, since the temperature elsewhere is constant (250°C in the filter zone). An increase in the UO_2 charge weight also causes the BrF_5 utilization efficiency to increase.

5. Favorable Fluorination Conditions

To improve the UF_6 production rate and BrF_5 utilization efficiency, a favorable combination of conditions (within the ranges of those studied) is: temperature = 300°C , inlet BrF_5 partial pressure = 0.29 atm, gas velocity = 0.89 ft/sec, and UO_2 charge = 4.4 kg. The use of either size of alumina (48 to 100 mesh or -100 mesh) and the presence or absence of fission-product compounds should not significantly affect these results. This combination of high temperature, high BrF_5 partial pressure, high velocity, and large UO_2 charge was not tested experimentally. On the basis of the calculated effects, one can predict with reasonable confidence that these conditions would give UF_6 production rates and BrF_5 utilization efficiencies approaching those shown in Table XVI. These UF_6 production rates and utilization efficiencies are considered highly acceptable for process application.

TABLE XVI. Average Total UF_6 Production Rate and BrF_5 Utilization Efficiency Predicted at a Favorable Combination of Levels of Independent Variables

Variable	Favorable Level		
Temperature	300°C		
BrF_5 partial pressure	0.29 atm		
Superficial gas velocity	0.89 ft/sec		
UO_2 charge	4.4 kg		
Alumina mesh	(48 to 100) or (-100)		
Fission products	Present or absent		

	Fraction of Uranium Reacted, F		
	0.50	0.667	0.75
Average total UF_6 production rate, lb/hr	9.5	9.1	8.4
lb/(hr)(ft ²)	185	177	164
Average total BrF_5 utilization efficiency, %	75	67	60

6. In-line Gas Analysis

The total production rate of UF_6 was monitored using three analytical techniques. In one technique, the off-gas from the reactor was instantaneously sampled at predetermined times and the hydrolyzed samples were analyzed chemically to obtain the fluorine, bromine, and uranium content. The other two techniques were based on the assumption that fluorination of U_3O_8 with BrF_5 produces oxygen and free bromine stoichiometrically. The oxygen concentration and the bromine concentration in the off-gas were monitored using a Hays oxygen analyzer and a Dupont Photometric analyzer, respectively.

Figures 8 and 9 compare the total UF_6 production rates and total BrF_5 utilization efficiencies obtained with the oxygen analyzer and off-gas samples for Run 5. Generally, the data are in good agreement throughout the run. The accuracy of the oxygen analyzer is better during the BrF_5 step than during the oxidation step because larger concentration differences are measured in the BrF_5 step. However, the values for UF_6 production rate and BrF_5 utilization efficiency obtained from the oxygen analyzer may be biased because of the possible presence of intermediate reaction products, UO_2F_2 and UF_4 . Therefore, the oxygen production rate may not correspond exactly to the UF_6 production rate and the associated BrF_5 utilization efficiency.

Fig. 8
 UF_6 Production Rate Based on
 Data from Oxygen Analyzer
 and Off-gas Samples (BrF_5
 Step of Run 5)

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Fig. 9
 BrF_5 Utilization Efficiency
 Based on Data from Oxygen
 Analyzer and Off-gas Samples
 (BrF_5 Step of Run 5)

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The output obtained in the continuous analysis for bromine with the photometric analyzer was smooth and indicated a uniformly decreasing rate of bromine production after an initial peak rate. However, no quantitative calculations could be made since the photometric analyzer gave a nonlinear output as a function of bromine concentration. The nonlinear output was ascribed to poor isolation of the 546-m μ measuring wavelength. From the qualitative appearance of the output, it has been concluded that this instrument (with an added isolation filter) can be used for continuous monitoring of the U_3O_8 - BrF_5 reaction. The formation of intermediate products such as UO_2F_2 and UF_4 may affect the relative rates of bromine evolution and UF_6 production.

C. Agglomerates in the Bed

In the runs in which fission products were added, small quantities (less than 50 g) of agglomerates were found in the final reactor beds. The appearance of the agglomerates was not the same in all runs. In some runs, hard 1/4- to 3/4-in. "lumps" were found. In other runs, soft 3/8-in. "nuggets" were found that were yellow inside. Spectrochemical analysis

was performed on samples of the final alumina beds, the "lumps," and the "nuggets." Alumina was the major component of both forms of agglomerates.

With regard to the fission products, the following comparisons were made:

1. Comparison of nugget composition with fluid-bed composition. Nuggets contained more cesium, molybdenum, and rubidium, with rubidium concentration differing the most.
2. Comparison of lumps to fluid bed. Lumps contained more barium, cesium, molybdenum, and rubidium.
3. Comparison of lumps to nuggets. Lumps contained more barium and less rubidium.

In conclusion, both forms of agglomerates appear to have formed in the presence of the fission-product compounds. The fact that the fission-product compounds were added to the system as fine oxide or fluoride powders may have contributed to agglomerate formation. The presence of agglomerates did not hinder removal of the remainder of the alumina beds, and the uranium loss to the agglomerates was considered small.

D. Automatic Filter Blowback

A system for automatically blowing the accumulated fines from the sintered-metal filters kept the pressure drop across the four filters to less than 0.4 psi. The system used solenoid valves (with 0.125-in. orifices) mounted within 5-6 in. of the filter outlets. Each of the four filters was blown back with a 1.5-sec pulse of 80-psi nitrogen every 24 min. The individual pulses were timed so that one of the filters was blown back every 6 min. Inspection of the record of the filter pressure drop showed that only three of the four filters were being efficiently cleaned of fines. This observation was confirmed by visual inspection of the filters at the end of the experiment. The filter that was not efficiently cleaned was constructed of nickel with a 5- μ pore diameter. The other nickel filter, also of 5- μ pore diameter, and both 10- μ pore-diameter Monel filters were well cleaned. The off-gas lines downstream from the filters were free of fine solids at all times.

V. CONCLUSIONS

The engineering-scale study of oxidation of UO_2 followed by BrF_5 fluorination of U_3O_8 fines has demonstrated that high reaction rates and high reagent utilizations can be achieved under various operating conditions. Operational problems such as bed sintering experienced when fluorine was used as the fluorinating agent have been eliminated by using BrF_5 as the fluorinating agent.

Measurement of the effects of operating variables indicates that UF_6 production rates up to $164 \text{ lb}/(\text{hr})(\text{ft}^2)$ and BrF_5 utilization efficiencies up to 75% for reacting the first 50% of the uranium charge can be expected at the following operating conditions:

	Oxidation Step	BrF_5 Fluorination Step
Temperature, $^{\circ}\text{C}$	450 ^a	300
Concentration	19.2 v/o ^a O_2 in N_2	0.29 atm BrF_5 in N_2
Superficial gas velocity, ft/sec	1.4 ^a	0.89
UO_2 charge, kg	4.4	4.4
Alumina particle size, mesh	-100	-100 or 48 to 100
Fission products	Present or absent	Present or absent

^aNot varied in this work.

The qualitative and quantitative results of this pilot-scale study are in good agreement with the bench-scale work of Gabor and Ramaswami³ and Anastasia⁴ and the laboratory-scale studies of Jarry.¹ The UF_6 production rates and BrF_5 utilization efficiencies predicted for favorable operating conditions are considered highly acceptable for process application.

APPENDIX A

Chemical Pulverization of Spent Uranium Dioxide (Literature Survey)1. Introduction

The fluoride-volatility processing¹⁰ techniques under development for the reprocessing of composites of low-enrichment, light-water-reactor fuel and fast-reactor oxide fuel aim at volatilization of the hexafluorides of uranium and plutonium by simple gas-solid halogenation reactions. In the preparation of fuel pins, the uranium oxide is sintered to a theoretical density of 95-96% to achieve satisfactory fuel performance with respect to dimensional stability and retention of fission products during irradiation. The surface area of the UO_2 particles is a function of the sintered density of UO_2 pellets.¹¹ Because of the small surface area of sintered pellets, the reaction rate in subsequent fluoride-volatility processing will be low. In a solid-gas reaction, the optimum reaction rate is a primary function of the available interfacial area.

The Zircaloy-clad UO_2 fuel is declad by hydrochlorination, and the stainless steel-clad UO_2 fuel is declad with HF-O_2 mixture. The declad fuel is usually fragmented as a result of the severe stresses developed during reactor irradiation, fission-product inclusion, and fission-gas release. The fragmentation may not be extensive enough to enhance fluoride volatilization. Some of the latest fuel concepts aim at maintaining a molten pool of UO_2 at the fuel center. This axial fusion results in recrystallization of those portions, decreasing the closed porosity of the fuel and preventing to some extent the fragmentation into smaller pieces. Hence, comminution of the spent fuel will be necessary in order to obtain high rates for the fluorination of uranium and plutonium with fluorine or an interhalogen such as BrF_5 or ClF_3 .

Dry and wet mechanical pulverizing techniques are not desirable for spent-fuel application because they incur high costs of remote handling. Therefore, oxidation of the spent UO_2 , yielding highly reactive U_3O_8 fines, has been advocated as a step to precede fluorination. Exploratory experiments on the oxidation of sintered UO_2 fuels have been carried out in connection with at least two fuel-processing techniques. For the fluoride-volatility process, the low-temperature chemical pulverization of the UO_2 not only produces highly reactive U_3O_8 fines, but also permits redistribution of the large amount of heat¹² from fines to the fluid bed, rather than from pellets to the fluid bed as in the direct fluorination of UO_2 pellets. This is shown in the following reactions:

Direct fluorination of packed bed of pellets

$$\Delta H_{298^\circ\text{C}} = -257 \text{ kcal/mole}^{13}$$

Oxidation of packed bed of pellets

$$\Delta H_{298^\circ \text{C}} = -25 \text{ kcal/mole}^{13}$$

Fluorination of U_3O_8 fines

$$\Delta H_{298^\circ \text{C}} = -237 \text{ kcal/mole}^{13}$$

In an alternative fluorination procedure, bromine pentafluoride selectively reacts with U_3O_8 , forming UF_6 , thus permitting a separation of uranium from plutonium.¹⁴ The separation reaction is

This appendix reviews oxidation of uranium oxide and the influence of the reactor processes to predict the oxidation characteristics of the spent UO_2 fuel. The discussion is organized under the following headings:

- a. Properties of spent fuel.
- b. Chemistry of the oxidation of pure UO_2 to U_3O_8 .
- c. Parameters influencing the oxidation of spent UO_2 fuel.
- d. Volatilization of ruthenium and other fission products during oxidation of the spent fuel.
- e. Chemical pulverization of spent UO_2 .

2. Properties of Spent Fuel

The properties of the irradiated uranium dioxide fuel will differ from those of the original ceramic fuel. The fuel discharged from the light-water reactors will have a PuO_2 content of ~1-2 w/o and a total fission-product accumulation of ~0.25 w/o.¹⁵ The fuels discharged from a fast reactor will contain 15-25% plutonium, depending upon the reactor zone in which irradiation occurred. Further, the fuel will have been annealed during irradiation.

Reactor irradiation causes both macro- and microstructural changes in UO_2 fuel.¹⁶ The extent of modification is mainly dependent upon such interrelated factors as (1) time inside the reactor, (2) level of exposure, (3) fuel operating temperature, (4) fission-product accumulation and swelling caused by the generation of fission gas, and (5) initial pellet density and microstructural characteristics. The fuel discharged from a power reactor

is normally cooled for a period of time to let certain hard, short-lived activities decay. In some of the recent fuel concepts, maintenance of a thin molten section in the ceramic core during reactor operation has been advocated to obtain higher power density and power output.

Unirradiated sintered UO_2 has a typical grain diameter of 5-15 microns, and the porosity is randomly distributed.¹⁷ Irradiation causes finer grains of 1 micron or less in size. The temperature of the fuel core is maintained at ~1700-2800°C (below the melting point of UO_2) during reactor irradiation, and the postirradiation microstructure is heavily influenced by this annealing treatment. The annealing treatment produces columnar grain growth. If the fuel is allowed to fuse axially, the grains on cooling segregate and relocate themselves. Further, axial fusion gives rise to closely packed, dense UO_2 crystals.

Gross fission-product migration and relocation take place in the sintered UO_2 pellets during high-temperature irradiation.^{18,19} The extent of relocation is a function of the level of exposure, heat-generation rate, and the resulting temperature gradient. Bates¹⁸ related fission-product and plutonium migration to the microstructure of UO_2 formed during irradiation. He observed that the distribution and axial concentration vary markedly between fission products. Cesium and ruthenium show the greatest tendency to migrate; ^{95}Zr - ^{95}Nb and cerium-praseodymium have the least tendency to migrate. The axial concentration of cesium has varied as much as 1000-fold. Plutonium also has migrated during irradiation of the pellet. Study of the microstructure of UO_2 samples having a simulated 0-10% fission content has shown that the fission products mainly concentrate on the grain boundaries of the UO_2 .

3. Chemistry of the Oxidation of Pure UO_2 to U_3O_8

The many experiments on the oxidation of UO_2 to U_3O_8 have yielded considerable data on the kinetics of oxidation of UO_2 , the number and the structure of the phases formed, the extent of solid solubility between the phases, the thermodynamic stability of the phases, and the mechanism of oxidation. Nevertheless, a universally acceptable theory of oxidation of UO_2 has not been evolved due to significant variations in the oxidation characteristics of UO_2 and the experimental conditions studied. A number of experimental techniques such as rate data, DTA, TGA, X-ray diffraction, electron and neutron diffraction, and magnetic-susceptibility measurements have been used to elucidate the oxidation phenomena. The major reason for results differing significantly is thought to be differences in the specific surface area of the UO_2 particles started with, which in turn are influenced by the preparatory history of UO_2 . The sintering characteristics of the UO_2 pellets depend on preparatory history.²⁰

A comprehensive monograph by Belle and Aronson²¹ identified the following three distinct processes of oxidation of UO_2 based on the temperature of oxidation: (a) chemisorption of oxygen at -183°C , (b) oxidation at temperatures of -30 to 50°C , obeying a logarithmic law, and (c) a more extensive bulk oxidation above 50°C .

Oxidation of UO_2 to U_3O_8 takes place only in the high-temperature region. Several experiments²¹ have indicated that conversion of UO_2 to U_3O_8 takes place in two stages: (a) oxidation of cubic UO_2 to a tetragonal oxide of composition $\text{UO}_{2.25}$ or $\text{UO}_{2.37}$ below 250°C , and (b) oxidation of the tetragonal oxide to an orthorhombic U_3O_8 above 250°C . Complete conversion of UO_2 to U_3O_8 takes place only above 375°C . There has been disagreement with respect to which intermediate oxides of uranium form, namely, U_3O_7 or U_4O_9 . This section has dealt with the mechanism of the oxidation of UO_2 to intermediate oxides of uranium (U_3O_7 or U_4O_9) to a major extent, since there is good agreement regarding the conversion of UO_2 to U_3O_8 above 375°C .

a. Phase Equilibria

Hoekstra and Belle²² reviewed the different phase diagrams proposed for conversion of the cubic phase ($a = 5.471 \text{ \AA}$) to the tetragonal phase. Many authors have identified two stoichiometric compositions, viz., U_3O_7 and U_4O_9 , as representatives of the tetragonal phase. In some experiments, transition to the tetragonal phase and the compositions U_3O_7 and U_4O_9 has not been observed because of the vast nonstoichiometry exhibited by UO_2 during oxidation, depending on the preparatory history. Hoekstra *et al.*²³ suggested that at low temperatures ($\sim 160^\circ\text{C}$) and with very active (high surface area/unit mass) UO_2 powders, the tetragonal phase forms. They also observed that U_4O_9 is easily oxidized to U_3O_7 .

Based on equilibrium oxidation/reduction experiments carried out with CO/CO_2 mixtures, Sudo and Kogishi²⁴ identified four phases, UO_2 , U_4O_9 , U_3O_7 , and U_3O_8 , in the composition range UO_2 - U_3O_8 up to 1200°C . Above 580°C , solubility of oxygen in uranium dioxide increases with rising temperature; below 580°C , the solubility increases with decreasing temperature. The

TABLE XVII. Heats of Formation of Uranium Oxides

Uranium Oxide	$-\Delta H_{298^\circ\text{K}}$, kcal/mole
UO_2	259.2
U_4O_9	1078 ± 4
U_3O_7	815.7 ± 2 or 821 ± 2.1
U_3O_8	853.5

oxygen-rich phase of this region is heterogeneous and can be expressed as $\text{UO}_{2+x} + \text{U}_4\text{O}_9$. The upper limit of this region is 1073°C . In the composition range U_4O_9 - U_3O_8 , a homogeneous solid solution exists up to 1200°C .

The four oxides of uranium are thermodynamically stable. Their heats of formation are given in Table XVII.²⁵

b. Mechanism of Oxidation of UO_2

The oxidation of UO_2 to U_3O_8 has been the major area of dispute with respect to the interpretation of the kinetics. The consensus²¹ has been that the oxidation follows a diffusion-controlled process, since qualitatively many authors have obtained parabolic reaction rates. During oxidation, as seen in Table XVIII, the density of U_3O_7 has increased. This suggests that diffusion of oxygen can take place, either directly into the UO_2 body lattice without the formation of another phase, or through a tetragonal oxide layer of definite stoichiometry formed over the UO_2 particle. Although the X-ray data show some evidence for the formation of a diphasic compound, the kinetic data and the diffusion curves could not distinguish between the two processes. Magnetic susceptibility measurements and some X-ray data indicate that an interstitial mechanism is possible. Table XVIII²¹ indicates that there is no change in the surface area of the oxidized tetragonal oxide. Some recent work shows that the mechanism of oxidation is purely a function of the surface area of the UO_2 particle.

TABLE XVIII. Schematic Representation of Changes in Physical Properties during Oxidation of UO_2 to U_3O_8 ²¹

Properties	<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="border: 1px solid black; padding: 2px;">UO_2</div> <div style="text-align: center;"> Below 250°C </div> <div style="border: 1px solid black; padding: 2px;"> Tetragonal Oxide $\text{UO}_{2.25}-\text{UO}_{2.37}$ </div> <div style="text-align: center;"> Above 250°C </div> <div style="border: 1px solid black; padding: 2px;"> Orthorhombic U_3O_8 </div> </div>		
1. O/U ratio	2	2.25-2.37	2.67
2. Crystal lattice	Cubic	Tetragonal (?)	Orthorhombic
3. Density	10.89 g/cc	11.21 g/cc (11.4 g/cc)	8.35 g/cc
4. Surface area	0.6 m ² /g	No change	2.8 m ² /g (at 300°C)
5. Lattice spacing	a = 5.4683 Å	a/c = 1.031	
6. Possible compositions	-	U_3O_7 & U_4O_9	-

Smith²⁶ indicated that the oxidation of UO_2 to U_3O_8 is controlled by diffusion of oxygen through a tetragonal layer of U_3O_7 . He observed a rapid oxidation rate during the initial stages of reaction, followed by a constant oxidation rate. The initial rapid-rate period has been attributed to the absorption of oxygen on a previously deposited and chemisorbed layer of oxygen and the constant reaction-rate period to the diffusion of oxygen through a layer of U_3O_7 (or U_4O_9) of constant thickness 224 ± 72 Å. Harrison et al.²⁷ reported that any intermediate U_3O_7 layer was thin (probably <1000 Å thick) and that the oxidation process did not appear to be controlled by any diffusion process.

Scott and Harrison²⁸ showed that UO_2 powders of surface area greater than $1 \text{ m}^2/\text{g}$ exhibit a characteristic two-step reaction under linear heating rates in air. The first-step product has been identified as tetragonal U_3O_7 corresponding to an O/U ratio of 2.35 ± 0.02 in the range $74\text{--}340^\circ\text{C}$. The second-step oxidation leading to U_3O_8 goes to completion near 500°C four times as fast as U_3O_7 formation and is time-dependent. Low surface-area powders ($<0.05 \text{ m}^2/\text{g}$) of UO_2 have been directly oxidized to U_3O_8 ; the rates were similar to the rates for the second step with fine powders. The activation energy for the $\text{UO}_2\text{--U}_3\text{O}_7$ step was found to be 19.7 kcal/mole , which is comparable to other experimental values. Walker's²⁹ thermobalance tests showed that (a) with UO_2 powders of surface area greater than $2 \text{ m}^2/\text{g}$, the oxidation will be diffusion-controlled; (b) with UO_2 powders of surface area of $0.045 \text{ m}^2/\text{g}$, the oxidation proceeds via nucleation and growth; and (c) with UO_2 powders of intermediate surface area of $0.095 \text{ m}^2/\text{g}$, the oxidation process follows a hybrid of the above two mechanisms.

Peakall and Antill³⁰ carried out oxidation runs in a conventional thermobalance using UO_2 pellets of 0.98- or 0.89-cm diameter and a density of 10.5 g/cm^3 ; the pellets had been sintered in argon at 1450°C and in hydrogen-nitrogen mixture at 1400°C . The experiments, in the range $350\text{--}600^\circ\text{C}$, were characterized by an initial induction period similar to that noted in other observations. The experiments showed that the tendency to oxidation above 600°C is lower, probably due to the unstable nature of U_3O_8 above this temperature. The results of Peakall and Antill indicate that the oxidation rate of $14 \text{ mg}/(\text{cm}^2)(\text{hr})$ at 350°C increases to $51.7 \text{ mg}/(\text{cm}^2)(\text{hr})$ at 500°C , and falls gradually to $\sim 4.0 \text{ mg}/(\text{cm}^2)(\text{hr})$ at 900°C .

Belle and Aronson²¹ reviewed the effect of partial pressure of oxygen on the oxidation rate. Generally there is no significant change in the oxidation rate at pressures between 0.2 and 1.0 atm oxygen. The oxidation rate falls from $121 \times 10^{-16} \text{ mg}/(\text{cm}^2)(\text{sec})$ at 0.2 atm oxygen to $6.8 \times 10^{-16} \text{ mg}/(\text{cm}^2)(\text{sec})$ at 0.0007 atm oxygen. Large-scale studies at Atomics International³¹ and Mol³² confirmed that the oxidation rate obtained using air (0.2 atm oxygen) and pure oxygen is the same, except for increased agglomeration and more heat-transfer problems when a higher concentration of oxygen is used.

Belle and Aronson²¹ suggested that the oxidation of U_3O_7 to U_3O_8 follows an S-shaped path, indicating that this step follows a nucleation and growth mechanism.

Table XVIII indicates that enlargement of the unit cell from cubic UO_2 to orthorhombic U_3O_8 during oxidation is associated with a decrease in density from 10.89 to 8.35 g/cc , a fourfold increase in surface area, and a 30% increase in the specific volume, resulting in the chemical pulverization of UO_2 into high-surface-area U_3O_8 fines. The oxidation of UO_2 is influenced by the addition of foreign oxides, which form solid solutions with UO_2 .

4. Parameters Influencing the Oxidation of Spent UO_2 Fuel

Irradiation of UO_2 fuel affects its physicochemical and metallurgical properties. Hence the behavior of spent UO_2 fuel during oxidation should differ from the behavior of unirradiated fuel composites. This section discusses the following variables influencing the oxidation of the spent UO_2 fuel pellets:

- a) Effects of surface area, crystallinity, and density.
- b) Influence of temperature and oxygen partial pressure.
- c) Influence of presence of PuO_2 on oxidation of UO_2 .
- d) Influence of presence of fission products on oxidation of spent UO_2 fuel.
- e) Influence of irradiation annealing and axial fusion on oxidation of UO_2 .

a. Effects of Surface Area, Crystallinity, and Density

The uranium dioxide fuel is manufactured by powder-packing and high-temperature sintering techniques. Hence it can be concluded that the influences of surface area, crystallinity, and density are closely related. UO_2 pellets should have a density of 95-96% to effectively retain the fission products. Comparison of the oxidation behavior of pellets of 95-96% theoretical density with that of a monocrystal has shown that the rate of oxidation of a monocrystal is low. Comparison with less crystalline specimens has revealed that the rate of oxidation increases with an increase in noncrystallinity of the sample.³² Further, the monocrystal exhibits an initial induction period of no weight change before substantial oxidation starts.

A denser sample has less surface area and open porosity. Studies have shown that at 550°C UO_2 pellets of density ~10.4 g/cc oxidized at a reaction velocity of 0.59%/min, whereas a sample of density 9.7 g/cc oxidized at a reaction velocity of 0.71%/min.³²

It has also been observed that the density, crystallinity, and specific surface area of the sample affect the particle size of the U_3O_8 during chemical pulverization. Pellets of higher density produce more U_3O_8 fines than do loosely packed samples. Samples of 92-94% theoretical density produced 70.1% of +100 mesh U_3O_8 and 29.8% of -100 mesh U_3O_8 ; samples of 94-95% theoretical density produced 62.3% of +100 mesh U_3O_8 and 37.5% of -100 mesh U_3O_8 .³¹

b. Influence of Temperature and Oxygen Partial Pressure

Kinetics studies on the oxidation of UO_2 revealed that UO_2 is converted to U_3O_8 only above 250°C, and that for complete oxidation, temperatures of the order of 400-600°C are needed. The data obtained on the rate of

oxidation versus temperature³¹ indicate that although a high rate of oxidation is obtainable in the range 450-550°C, the temperature influences the particle size of the U_3O_8 fines produced. Maximum pulverization (reported as a measure of -400 mesh U_3O_8 particles produced) takes place at ~520°C (at low flowrate and low concentration of oxygen). This is attributed to a combination of higher reaction rates at elevated temperatures and the more effective pulverization which occurs at low temperatures. In other words, at higher temperatures, there seems to be more of a tendency for clinker formation (of U_3O_8). These observations indicate that only if sufficient heat removal from the reaction phase is achieved can clinker formation be avoided, since the oxidation of urania is an exothermic reaction.

The kinetics studies indicated that the effect of oxygen pressure on the oxidation rate is significant only at very low partial pressures. Studies at Atomic International³¹ indicate that pure oxygen results in rapid combustion of urania resulting in excursions to excessive temperatures and agglomeration of the U_3O_8 particles, whereas oxidation in air proceeds smoothly. The comminution efficiency during oxidation using air or an equivalent partial pressure of oxygen was nearly the same, and the presence of nitrogen helped heat removal from the reaction phase and thus lessened the tendency to agglomeration. In large-scale tests at the Mol,^{32,33} 10-50 v/o of oxygen yielded fine powders of U_3O_8 without much agglomeration.

c. Influence of Presence of PuO_2 on Oxidation of UO_2

Plutonium levels in the low-enriched UO_2 fuels discharged from a BWR or PWR system have been estimated to be of the order of 2% or less. For fast-reactor fuels, the plutonium content of the discharged blanket fuel will be 2-6%, and the plutonium content of the core fuel will be 15-25%. Work on the development of mixed-oxide fuels of plutonium and uranium has revealed that these two oxides form continuous solid-solution compounds. Studies of oxidation kinetics of such mixed oxide fuels have shown that the rate of oxidation is mainly determined by the composition of the fuel and the temperature of oxidation. Pure UO_2 undergoes small structural changes on oxidation in air at 100-350°C and major structural changes at higher temperatures, whereas PuO_2 under similar conditions does not absorb oxygen further into the crystal lattice. Gerrish and Halteman³⁴ observed that the oxidation of coprecipitated $(U,Pu)O_2$ in dry air at 140-500°C proceeds by a two-step reaction. In the first step, the oxide $(U,Pu)_3O_7$ is formed below 350°C and the oxide $(U,Pu)_4O_9$ at higher temperatures. The second step is the nucleation and growth of the oxide $(U,Pu)_3O_8$.

Brett and Fox³⁵ reported that either single-phase (cubic or orthorhombic) or two-phase (cubic and orthorhombic) products are formed during oxidation of $(U,Pu)O_2$, depending upon the composition. Although neither pure U_3O_8 nor pure PuO_2 has been observed, orthorhombic solid

solutions of M_3O_{8-x} type have been observed in the range 0-10 m/o PuO_2 , and cubic solid solutions of the MO_{2+x} type have been observed when 40-100 m/o PuO_2 was oxidized.

The oxidation of ~1-mg samples of $(U,Pu)O_2$ prepared by different methods has been studied at 375, 400, 425, 450, 475, and 500°C at Mol.³² The oxidation rate of UO_2 samples containing 10% or less PuO_2 was only slightly reduced due to the presence of plutonium, whereas samples containing 20% or more PuO_2 were not completely oxidized. Similar observations were also reported by Gerrish and Haltzman.³⁴ The oxide fuels discharged from the cores of fast reactors are expected to contain 15-25% PuO_2 . The oxidation characteristics of such samples containing high concentrations of plutonium will require further intense investigation. Evidently, the solid solutions formed with high PuO_2 and low UO_2 concentrations should have some influence on the fracturing of cubic UO_2 crystals. However, low enriched UO_2 fuels with low PuO_2 content can be easily oxidized, probably at a slightly higher temperature and with a slightly longer period of oxidation.

d. Influence of Presence of Fission Products on Oxidation of Spent UO_2 Fuel

The maximum fission-product buildup in the fuels discharged from the light-water reactors has been estimated to be of the order of 0.25 w/o, and the fuels discharged from a fast reactor may contain fission-product concentrations of 10% or higher. The solid fission products are located in the grain boundaries, and the volatiles such as xenon, krypton, and iodine at the lattice vacancies. Oxidation of UO_2 causes fracture of the cubic lattice. The trapped fission-product gas fraction can be expected to evolve during oxidation. Evolution of fission-product gases during oxidation necessitates removal of these hazardous gases from the off-gas stream.

The solid fission products are oxides of Mo, Zr, Ba, Nb, Ru, and rare-earth elements. Smith²⁶ extensively studied the kinetics of the oxidation of sintered samples of UO_2 containing 0.1-0.5 w/o nonradioactive fission products. The results indicate that fission-product addition does not alter the mechanism of UO_2 oxidation qualitatively even though the rate of oxidation is lowered. The presence of 0.1-5% fission in unirradiated UO_2 increases the activation energy for diffusion-controlled oxidation from 22 to 28 kcal/mole. The behavior of fission products is very much dependent on the O/U ratio of the fuel and on the oxygen potential of the environment in which the fuel is irradiated. Harrison et al.²⁷ studied the oxidation at 320-380°C and 1/3 atm pressure of UO_2 irradiated to burnups up to 9%. They found that the activation energy for the second stage increases from ~15 kcal/mole for unirradiated UO_2 to ~25 kcal/mole at ~9% burnup of all uranium atoms. They concluded that the oxidation is best described as a first-order reaction occurring in two stages, the rate constant being higher for the second stage.

The fission products will probably exhibit their own oxidation (and volatilization) behavior to a detectable extent, depending on the percent of fission products in the solid solutions of UO_2 - PuO_2 .

Batch oxidation experiments have been carried out at Mol³³ with simulated samples of different preparatory histories. Tests at 350, 425, and 500°C indicate that pure sintered UO_2 samples oxidize five times as fast as a UO_2 sample containing 2 w/o fission. These results, however, cannot be taken as conclusive since the experiments were conducted with milligram quantities of samples and the samples were not uniformly prepared. In an attempt to stabilize UO_2 against oxidation, several mixed oxides, such as UO_2 - MoO_3 and UO_2 - ZrO_2 , are being developed. Lanspersky and Vogaril³⁶ state that small additions of MoO_3 do not change the oxidation rate of UO_2 . They observed an activation energy of 23.5 kcal/mole for a pure UO_2 sample and 25.5 kcal/mole for UO_2 containing small amounts of MoO_3 . The difference is not significant. Vlasov and Bessonov³⁷ observed that a 6% addition of ZrO_2 markedly affects the second stage of oxidation (at 330°C); a change in the crystal structure occurs--either the appearance and growth of a new phase are facilitated, or its appearance is impeded by the formation of chemical compounds with the new-phase nuclei.

e. Influence of Irradiation Annealing and Axial Fusion on Oxidation of UO_2

Neutron irradiation of solids introduces structural faults in the macro- and microstructure. Any effect that impairs the crystal structure of UO_2 enhances the rate of oxidation of UO_2 . In studies at Mol, prior neutron irradiation significantly increased the oxidation of UO_2 by a factor of 1.5 at an oxidation temperature of 350°C, whereas at 425 and 500°C, the influence was less significant. Although irradiation improves the oxidation rate of pure sintered UO_2 , no effect was observed when fission products were present.

In the axially fused fuels, the tendency to form closely packed dense crystals of UO_2 is greater, and the extent of formation of solid solutions of UO_2 with PuO_2 and fission-product oxides increases. The relative absence of faults in this high-density crystalline section is detrimental to the oxidation phenomenon. In the interval between 25 and 75% reaction, axial fusion (with a simulated sample) decreases oxidation rate by a factor varying from 6.5 at 350°C to 1.2 at 500°C.

5. Volatilization of Ruthenium and Other Fission Products during Oxidation of the Spent Fuel

Ruthenium-103 (a fission product with a 40-day half-life and emitting a powerful gamma of 0.5 MeV) is largely separated from uranium and plutonium during oxidation of spent UO_2 fuels.³⁸ As the number of cycles of

oxidation and reduction of the fuel increases, the decontamination factor also increases. Analysis of samples in the off-gas filter indicated the presence of RuO_4 , suggesting that RuO_4 volatilizes during oxidation.

Baranev et al.³⁹ suggest that oxidation of RuO_2 is significant only above 700°C . This is also supported by the free energy of formation of RuO_2 and RuO_4 . The volatilization of RuO_4 can be catalyzed by chromic dioxide³⁹ at temperatures below 700°C . Therefore, it may be worth investigating whether Cr_2O_3 produced in the bed during destructive oxidation of stainless steel-clad fast-reactor fuels is a catalyst for the volatilization of ruthenium. If a significant amount of volatilization occurs, the addition of a small amount of Cr_2O_3 to the Zircaloy-clad fuel pellets prior to oxidation may be desirable.

6. Chemical Pulverization of Spent UO_2

a. Introduction

On the basis of the foregoing discussion, the equipment for chemical comminution of UO_2 pellets should be selected to meet the following process requirement: An efficient heat-transport mechanism should be assured, since the oxidation of UO_2 is an exothermic reaction and the reaction is very much temperature-sensitive; i.e., the reaction proceeds to completion only near $450\text{--}500^\circ\text{C}$, and temperatures above 700°C do not improve the yield.

Oxidation of UO_2 to U_3O_8 results in attrition of the pellet. In the fluoride-volatility process, maximum attrition is desired to increase plant throughput during the subsequent volatilization of uranium. Above 520°C , there is excessive agglomeration of the oxidized material, whereas at 520°C , attrition is at a maximum. The optimum oxidation rate should be achieved at $450\text{--}520^\circ\text{C}$.

Applicability to the fluoride-volatility process of equipment developed for the oxidative decladding of irradiated fuels is discussed in Subsection b below.

b. Oxidative Decladding of Fuels

The equipment developed for the Airox⁴⁰⁻⁴⁵ and Salt Cycle⁴⁶ processes consists of batch-oxidation units. The clad fuel rod (punctured at various places) is suspended in a resistance- or induction-heated furnace, and a stream of nitrogen and oxygen is directed over the fuel rod. The cladding bulges out due to oxidation of UO_2 pellets, and U_3O_8 is collected at the bottom of the reactor. This equipment is not suitable for application to the fluoride-volatility process since there is too great a tendency to agglomeration in the absence of efficient temperature control.

Baerns⁴⁷ studied the use of a fluidized-packed bed for carrying out the above oxidative decladding. Similar equipment is presently being used for studies in the fluoride-volatility process studies. The conclusions he reached will be discussed in Section 7 below.

7. Volatility Processes

Initial studies at Mol^{32,33} were carried out using a continuous vertical static-bed reactor in which UO_2 pellets were stacked over a grid. The pellets were externally heated to the reaction temperature. Air or mixtures of nitrogen and oxygen were passed through the bed from the top of the reactor. U_3O_8 powders formed, and mechanical vibration imparted to the reactor wall facilitated collection of the powder at the bottom of the reactor (under the support grid). When necessary, the reactor was operable continuously by feeding UO_2 pellets from the top. This equipment facilitated the removal of powder from the reaction zone and permitted direct easy control of the reaction, but there was more tendency to agglomeration than in a fluid-bed reactor. When pellets were oxidized at 450°C , $>99\%$ conversion was obtained, but the specific surface area of the particles was found to be less than $\sim 0.54 \text{ m}^2/\text{g}$, and the average diameter greater than $\sim 40 \mu$.

Presently, the oxidation step in the fluoride-volatility process is being carried out in a fluid-bed (alumina grains) reactor, at ANL⁴⁸ and at Mol.³³ Such a choice was probably made because the formation of volatile fluorides from U_3O_8 and PuO_2 involves highly exothermic reactions demanding good heat transfer. Performance of the oxidation of UO_2 and the fluorination of U_3O_8 in the same reactor poses no specific problems of material selection or corrosion and avoids the use of separate oxidation equipment.

Preliminary small-scale tests at Mol^{32,33} in a 5.5-cm-diam reactor indicated that a fluid-bed reactor is suitable for the oxidation of UO_2 . In a 5.5-cm-diam reactor and a 7-cm-diam reactor, temperature control of $\pm 50^\circ\text{C}$ within the bed was achieved. The method of manufacture of UO_2 and its physical characteristics strongly influence the required oxidation conditions such as time, temperature, and oxygen concentration. Studies of the influence of gas velocity on the time required for oxidation of a 700-800-g charge at 450°C in air indicated that a 2.5-3.0-ft/sec gas velocity at 450°C gives optimum conversion without much agglomeration. Reaction time is much reduced, at least by a factor of 3.5, when the velocity is increased from 0.26 to 0.92 ft/sec. Similarly, the time of reaction decreases with increased temperature, again with a greater tendency to agglomeration. Relatively high gas velocities (for example, 0.82 ft/sec measured at 20°C) are recommended to reduce the probability that agglomerates will form. However, the selection of each operating condition will depend mainly on the pellet history. In the experiments at ANL, gas velocities of the order of 0.2-1 ft/sec (at 20°C) were used during oxidation without any agglomeration.

The use of alumina in the fluidized bed helps to transport heat out of the reaction zone. A weight ratio of $\text{Al}_2\text{O}_3/\text{UO}_2 = 1$ has been recommended for oxidation. Changing from a 5.5-cm-diam reactor to a 7-cm-diam reactor affects the production rate and the oxidation time. In fluid-bed reactors, a small percentage of UO_2 has always been present after the reaction. This may be attributed to nonuniformity of bed mixing. Even though no temperature-excursion problems have been reported as a result of changing from a 5.5- to a 7-cm-diam column, the observations at ANL with a 3-in.-diam column indicate that a 100°C rise is possible. ORNL reported a temperature rise from 500 to 1038 and 793°C in two different experiments with a 5-in.-diam fluid-bed reactor.⁴⁹

In a fluidized-packed-bed reactor (where the oxidation of UO_2 is carried out), the mixing efficiency is poorer⁵⁰ and hence the heat-transfer characteristics are poorer. Baerns⁴⁷ concluded from his studies on oxidative decladding that in such fluidized-packed beds a more uniform temperature can be achieved (1) by increasing the gas velocity to elutriate the fines from the fluidized-packed bed, (2) by increasing the percentage of inert material in the fluidized bed, (3) by gas pulsing, and (4) by introducing mechanical vibration. Heat generation and temperature rise in large fluidized beds can also be kept at a minimum by controlled continuous addition of pellets to the reactor when the oxidation is in progress. This will allow maintenance of a higher percentage of alumina in the bed during the initial period, as suggested by Baerns. Near the end of the oxidation step, when the bed is enriched with a higher percentage of U_3O_8 particles, the fluidization characteristics may be different. Studies at Mol indicate that with an $\text{Al}_2\text{O}_3/\text{U}_3\text{O}_8$ ratio in the range of 0.82 to 1.1 and with U_3O_8 of $12\ \mu$ and Al_2O_3 of $110\ \mu$ diameter, relatively good homogeneity is observed; with alumina of 80 and $60\ \mu$ diameter, some nonhomogeneity in the U_3O_8 concentration in the bed is possible.

APPENDIX B

Corrosion of Nickel Equipment1. Fluid-bed Data

As part of this investigation, a corrosion study was performed in which the processing scheme consisted of (1) prefluorination of the alumina bed, (2) oxidation of uranium dioxide, and (3) fluorination of U_3O_8 using bromine pentafluoride. To investigate the cumulative process corrosion, three corrosion specimens of nickel-200 were placed at different locations (as shown in Fig. 10) inside a 3-in.-diam all-nickel reactor during eight runs of the program.

Each corrosion coupon was machined to 0.24-in. diameter and 1-in. length and inserted in the reactor on the end of a 0.25-in.-diam rod. The specimens, each weighing about 7-8 g, were cleaned and degreased before insertion in the reactor. After being exposed in eight runs, the coupons were removed and descaled in a molten-salt bath of equimolar $NaNO_3$ - KNO_3 at 500°C for 1-2 hr. The coupons were then quenched in water, cleaned, dried, and weighed. The corrosion rate of nickel was calculated using the formula

$$\text{mils/yr} = \frac{\text{g loss}}{(\text{in.}^2)(\text{hr})} \times \frac{\text{cm}^3}{8.91 \text{ g}} \times \frac{\text{in.}^3}{(2.54 \text{ cm})^3} \times \frac{10^3 \text{ mils}}{\text{in.}} \times \frac{8760 \text{ hr.}}{\text{yr}}.$$

Table XIX gives the exposure conditions of the three specimens and the observed corrosion rates. The corrosion rates, 14-19 mils/yr in the

TABLE XIX. Exposure Conditions and Corrosion Rates
of Nickel-200 Coupons

	Coupon 1	Coupon 2	Coupon 3
<u>Position in Reactor</u>	36 in. from bottom, in the fluidized bed	54 in. from bottom, in the fluidized bed	Filter zone
<u>Cumulative Treatment</u>			
1. 16-hr prefluorination with 5 v/o F_2 - N_2	550°C	550°C	250°C
2. 68-hr oxidation with 19.2 v/o O_2 - N_2	450°C	450°C	250°C
3. 27-hr fluorination with 11.1 to 20.7 v/o BrF_5 - N_2	225-300°C ^a	225-300°C ^a	250°C
<u>Corrosion Rate (mils/yr)</u>	19 ^b	14	0.6

^aDuring one experiment, the temperature in the fluidized bed rose rapidly to 465°C and then returned to normal.

^bSince the sample was damaged during descaling, the weight of scale was determined from Coupon 2.

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Fig. 10. Photomicrographs of Nickel-200 Corrosion Coupons

bed and less than 1.0 mil/yr in the filter zone, are comparable to the results obtained for nickel in other fluid-bed fluoride-volatility processing equipment.⁵¹ Photomicrographs of the descaled corrosion coupons, presented in Fig. 10, show no evidence of intergranular modifications.

Coupons 1 and 2, which were submerged in the fluidized bed showed higher corrosion than Coupon 3, which was placed near the filters in the disengaging section (held at 250°C for all processing steps).

2. Corrosion of Nickel Scrubber by Off-gas

The off-gas streams produced during prefluorination of the alumina bed and during fluorination of U_3O_8 using bromine pentafluoride were scrubbed with KOH solution (containing 0.05N KI to promote reaction) in an 8-in.-diam nickel tower. The waste-gas stream scrubbed during the prefluorination step consisted of ~5 v/o fluorine-nitrogen mixture. The waste-gas stream produced during the BrF_5 reaction consisted of BrF_5 (up to 20 v/o), bromine (up to 10 v/o), oxygen, and nitrogen. The waste gases were admitted into the nickel scrub tower through a 2-in.-diam nickel entry port near the top of the tower. As the gases entered the tower at the entry port, they were immediately washed down by a caustic spray from the top of the tower.

After about eight runs with alternate exposure to fluorine and BrF_5 , severe corrosion failure was observed near the entry port to the scrub tower (i.e., at the halogen gas-caustic solution mixing region). The holes formed at the nickel entry port are shown in Fig. 11. This corrosion failure of the nickel might have been caused by any or all of the following reasons: (1) localized hot spots during hydrolysis of bromine pentafluoride, neutralization of the halogens and the alkali, and the presence of the corrosive halogens at the reaction temperature, (2) wet bromine vapor, and (3) wet fluorine vapor.

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Fig. 11. Corrosion of Nickel Inlet Pipe to Off-gas Scrubber

into the center of the 8-in.-diam pipe. No problems have been observed with this arrangement.

Similar excessive corrosion of the stainless steel entry port near the gas-liquid mixing region occurred during the disposal of fluorine and BrF_5 with KOH-KI solution at ORNL.⁵²

The scrubber now uses an entry tube of Teflon, which extends

APPENDIX C

BrF₅ Inlet-gas Analysis

Inlet-gas samples were taken periodically during the BrF₅ fluorination step of the runs. The sampling equipment and procedure are described in Section II.D of this report. These samples were taken to check, from the ratio of bromine to fluorine, whether or not BrF₅ was the compound actually fed to the reactor. Table XX gives the Br/F ratios for the inlet-gas samples. Results of two of the runs are statistically invalid.⁵³ The mean ratio for the remaining samples was 0.834, compared to stoichiometric BrF₅, which is 0.841. A possible impurity, BrF₃, has a Br/F ratio of 1.402. However, the 95% confidence limit on the measured results was ± 0.141 ; therefore, all the valid results are within the experimental error for stoichiometric BrF₅.

TABLE XX. Br/F Ratios in the Inlet-gas Samples

Run	Sample Time, min	Br/F	Run	Sample Time, min	Br/F
3	20	0.828	9	15	1.300
3	180	0.821	9	175	0.950
4	15	0.838	10	15	0.944
4	175	0.709	10	175	0.826
5	20	0.870	11	20	0.658
5	360	0.863	11	180	0.793
6	15	0.840	Theoretical ratio		0.841
6	115	0.873	Average, all runs		0.848
7A	20	0.814	Average, all runs except		
7A	175	0.808	Run 9 (15-min sample)		
7B	20	0.748	and Run 11 (20-min sample)		0.834
7B	175	0.730	Final standard error, SE = 0.0642		
8	18	0.877	95% confidence limits = ± 0.141		
8	237	0.881			

APPENDIX D

Sieve Analysis

The sieve analyses of the crushed UO_2 pellets and the -48 +100 mesh and -100 mesh Al_2O_3 are as follows:

Crushed UO_2 Pellets		Alcoa T-61 Alumina		
			-45 +100 Nominal Mesh, w/o	-100 Nominal Mesh, w/o
Sieve	w/o	Sieve		
+7/16	14.07	+48	0.15	0
+5/16	29.53	+60	7.27	0
+5	33.97	+80	57.10	0.1
+6	3.80	+120	30.00	6.1
+7	3.71	+170	4.40	17.5
+10	7.53	+230	0.55	12.7
+14	3.67	+325	0.45	39.6
+18	2.42	Pan	0.20	24.0
Pan	1.61	Average diameter	179 μ	45 μ

APPENDIX E

Error Analysis of Bed Sample

The concentration of uranium in the fluidized bed at the end of the BrF_5 fluorination step was determined in two ways: (1) A grab sample was taken with the bed fluidized as described in Section II.D, and (2) the total fluidized bed was discharged and riffled to obtain a small representative sample.

The total fluid-bed (riffled) samples were considered the more representative, and the grab-sample results were compared with these data (as shown in Table XXI). Within 95% confidence limits, the concentration of uranium in the grab samples was within $\pm 126\%$ of the concentration in the fluid bed (riffled samples) at the end of the BrF_5 fluorination. This agreement is good, since uranium concentrations in the bed at the end of the runs were relatively low.

TABLE XXI. Comparison of Concentration of Uranium in Final Grab Samples and in Final Fluid-bed Samples

Run	Uranium in the Final Samples, w/o			$\frac{(\text{Grab}) - (\text{Fluid Bed}) \times 100}{\text{Fluid Bed}} =$
	Grab	Total Fluid Bed	$(\text{Grab}) - (\text{Fluid Bed})$	% difference
3	0.0510	0.0492	0.0018	3.66
4	0.0425	0.0158	0.0267	168.99
5	0.4250	0.4530	-0.0280	-6.18
6	0.2190	0.1730	0.0460	26.59
7A	0.4200	0.5000	-0.0800	-16.00
7B	0.2400	0.1810	0.0590	32.60
8	0.1460	0.2700	-0.1240	-45.93
9	0.1710	0.0620	0.1090	175.81
10	0.1340	0.1240	0.0100	8.06
11	0.0422	0.0444	-0.0022	-4.95
Standard Error = 56%				

APPENDIX F

Examples of Calculations and Error Analysis

The effects of the independent variables on the average UF_6 production rate were calculated for: (1) rates in the entire system, (2) rates in the fluid bed only, and (3) rates "elsewhere" (UF_6 produced at sites in the system other than the fluid bed; for example, in the filter section).

1. Calculation of the Effects of the Independent Variables on the Average UF_6 Production Rate of the Entire System

Calculation of the effect of the variables on the total UF_6 production rates required the following steps:

- 1) Calculation of the theoretical total UF_6 produced during a run.
- 2) Calculation of the instantaneous UF_6 production rates in the entire system from the bromine and fluorine content of the off-gas samples.
- 3) Correction of the total UF_6 production rates to conform to the theoretical UF_6 value.
- 4) Calculation of F, the ratio of uranium converted to UF_6 to uranium available for fluorination.
- 5) Calculation of the average UF_6 production rate to any value of F.
- 6) Correction for variations in the partial pressure of the BrF_5 fed and for variations in the fluidizing velocity.

a. Calculation of TU, the Theoretical Total UF_6 Produced

The theoretical UF_6 produced in a run, TU, is UF_C , the uranium charged (converted to pounds of UF_6), minus UF_R , the sum of the uranium removed in bed samples and the uranium retained by the Al_2O_3 (converted to pounds of UF_6). That is,

$$\text{TU} = \text{UF}_C - \text{UF}_R \quad (\text{F.1})$$

Example 1. Run 4. Theoretical total UF_6 produced.

$\text{UF}_C = 12.51 \text{ lb of } \text{UF}_6 \text{ (from run data).}$

$\text{US} = 0.26 \text{ lb of } \text{UF}_6 \text{ removed in samples (from run data).}$

$\text{UB} = 0.013 \text{ lb of } \text{UF}_6 \text{ retained by } \text{Al}_2\text{O}_3 \text{ beds (from run data).}$

$$UF_R = UB + US = 0.27 \text{ lb of } UF_6.$$

$$UT = UF_C - UF_R = 12.51 - 0.27 = 12.24 \text{ lb of } UF_6.$$

b. Calculation of IR, the Instantaneous Total UF_6 Production Rate from the Bromine and Fluorine Content of Off-gas Samples

The instantaneous total UF_6 production rate, IR, can be obtained from a knowledge of the U/F and U/Br ratios for the material collected in the off-gas sample bulbs. If it is assumed that the fluorine or bromine in the off-gas comes only from the BrF_5 feed, the instantaneous UF_6 production rate can be related to the BrF_5 feed rate by the following equations, based on the stoichiometry of the reaction:

Fluorine Basis

$$IR = \frac{U}{F}(47.88)(BrF_5 \text{ feed rate})(0.0168), \text{ lb/hr}$$

Bromine Basis

$$IR = \frac{U}{Br}(40.28)(BrF_5 \text{ feed rate})(0.0168), \text{ lb/hr}$$

The instantaneous total UF_6 production rate, IR, for a typical run (Run 4) on a bromine basis, was plotted against time (as shown in Fig. 12); when duplicate samples were taken, the average rate was plotted.

Fig. 12. Total UF_6 Production Rates Using Fluorine Basis for Run 4

c. Correction of the UF₆ Production Rate to the Theoretical UF₆ Value

To minimize the percent error arising from analysis and sampling techniques, the data obtained were compared with the theoretical value.

The theoretical total UF₆ produced, TU, was known (Eq. F.1). The total UF₆ produced, UP, is the sum of the incremental areas under the total UF₆ production-rate curve (obtained from a plot of the instantaneous production rates, as exemplified in Fig. 12). That is,

$$UP = \Delta A_1 + \Delta A_2 + \dots + \Delta A_n. \quad (F.2)$$

An incremental area, ΔA_n , is the average UF₆ production rate for the area, aR_n , multiplied by the time increment for the area, Δt_n :

$$\Delta A_n = aR_n \times \Delta t_n. \quad (F.3)$$

The average production rate for the incremental area, aR_n , is the average of the instantaneous rate, IR, at the start and end of Δt_n :

$$aR_n = \frac{IR_{sn} + IR_{en}}{2}. \quad (F.4)$$

The time increment, Δt_n , of the incremental area is the difference between the times, t , at the end and start of the area:

$$\Delta t_n = t_{en} - t_{sn}. \quad (F.5)$$

Substituting Eqs. F.4 and F.5 into Eq. F.3, we have

$$\Delta A_n = \frac{IR_{sn} + IR_{en}}{2} (t_{en} - t_{sn}). \quad (F.6)$$

For the first incremental area, ΔA_1 , the instantaneous production rate at the start is unknown. The instantaneous rate at the end of the area, IR_{e1} , is assumed to be the average. Equation F.4 for the first incremental area then becomes

$$aR_1 = IR_{e1},$$

and Eq. F.6 becomes

$$\Delta A_1 = (IR_{e1})(t_{e1} - t_{s1}).$$

Example 2. Run 4. First incremental area, fluorine basis.

From Fig. 12,

$$IR_{e1} = 7.64 \text{ lb/hr}, \quad t_{e1} = 1/3 \text{ hr}, \quad \text{and} \quad t_{s1} = 0;$$

$$\Delta A_1 = IR_{e1}(t_{e1} - t_{s1}) = 7.64(1/3 - 0) = 2.55 \text{ lb.}$$

The remaining incremental areas are calculated using Eq. F.6.

Example 3. Run 4. Total UF_6 produced, fluorine basis.

$$UP = \Delta A_1 + \Delta A_2 + \Delta A_3 + \Delta A_4 + \Delta A_5 + \Delta A_6 \text{ (from Eq. F.2);}$$

$$\Delta A_1 = 2.55 \text{ (from Example 2).}$$

From Fig. 12 and Eq. F.6,

$$\Delta A_2 = \frac{IR_{s2} + IR_{e2}}{2} (t_{e2} - t_{s2}) = \frac{7.64 + 8.19}{2} (2/3 - 1/3) = 2.64 \text{ lb,}$$

$$\Delta A_3 = \frac{IR_{s3} + IR_{e3}}{2} (t_{e3} - t_{s3}) = \frac{8.19 + 6.53}{2} (1 - 2/3) = 2.45 \text{ lb,}$$

$$\Delta A_4 = \frac{IR_{s4} + IR_{e4}}{2} (t_{e4} - t_{s4}) = \frac{6.53 + 3.74}{2} (1\frac{2}{3} - 1) = 3.42 \text{ lb,}$$

$$\Delta A_5 = \frac{IR_{s5} + IR_{e5}}{2} (t_{e5} - t_{s5}) = \frac{3.74 + 0.02}{2} (2\frac{1}{3} - 1\frac{2}{3}) = 1.25 \text{ lb,}$$

$$\Delta A_6 = \frac{IR_{s6} + IR_{e6}}{2} (t_{e6} - t_{s6}) = \frac{0.02 + 0.02}{2} (3 - 2\frac{1}{3}) = 0.013 \text{ lb,}$$

and

$$UP = 2.55 + 2.64 + 2.45 + 3.42 + 1.25 + 0.013 = 12.32 \text{ lb.}$$

The total UF_6 produced, UP, should equal the theoretical total UF_6 produced, TU. However, sampling and analytical errors require a correction factor, C, to be applied to the total UF_6 produced to make it equivalent to the theoretical UF_6 produced.

$$TU = C(UP) \text{ or } C = \frac{TU}{UP} \quad (F.7)$$

Example 4. Run 4. Correction factor, fluorine basis.

TU = 12.24 lb (from Example 1);

UP = 12.32 lb (from Example 3);

$$C = \frac{12.24}{12.32} = 0.994.$$

Correction factors were calculated for all the runs for both the bromine and fluorine basis. To determine if one basis was better than the other, the average correction factors were compared.

Average correction factor (bromine basis): 1.092;

Average correction factor (fluorine basis): 1.086.

The differences were not considered significant, and the average of the correction factors obtained on a bromine and fluorine basis could be used in future calculations. However, in this case they were independently calculated for comparison.

The instantaneous total UF_6 production rates, IR, were multiplied by the correction factor, C, obtained by Eq. F.7 to make the area under the curve equivalent to the theoretical total UF_6 produced, TU. (Fig. 12, brokenline).

$$TU = C(UP) \text{ (Eq. F.7);}$$

$$C(UP) = C(\Delta A_1) + C(\Delta A_2) + \dots + C(\Delta A_n) \text{ (from Eq. F.2);}$$

$$C(\Delta A_n) = C \frac{IR_{sn} + IR_{en}}{2} (t_{en} - t_{sn}) \text{ (from Eq. F.6);}$$

$$C(\Delta A_n) = \frac{C(IR_{sn}) + C(IR_{en})}{2} (t_{en} - t_{sn}).$$

d. Calculation of F, the Ratio of UF_6 Produced to the Uranium (as UF_6) Available for Fluorination

To compare the total UF_6 production rates of the runs on a similar basis, the times at which certain fractions, F, of the uranium had reacted were calculated. F = the ratio of C(UP), the corrected total UF_6 produced, to UA, the uranium (as UF_6) available for fluorination.

At a given value of F, all of the runs could be compared on an equal basis.

$$F = \frac{C(UP)}{UA} \quad (F.8)$$

The UF_6 available, UA , equals TU , the theoretical total UF_6 produced, plus UB , the uranium retained by the Al_2O_3 beds (converted to pounds of UF_6).

$$UA = TU + UB. \quad (F.9)$$

Example 5. Run 4. UF_6 available, fluorine basis.

$TU = 12.24$ lb and $UB = 0.013$ lb (from Example 1);

$UA = 12.24 + 0.013 = 12.25$ lb (from Eq. F.9).

The F values were calculated at the times of sampling and plotted against time (as shown in Fig. 13).

Fig. 13. Plot of F , Fraction of Available Uranium Reacted for Run 4

Example 6. Run 4. F , at the time of the first sample, fluorine basis.

$UA = 12.25$ lb (from Example 5);

$C(UP)$ at the first sample = $C(\Delta A_1)$;

$C(\Delta A_1) = 2.55$ lb $\times$ 0.994 (from Examples 2 and 4);

$$F = \frac{2.55}{12.25} \times 0.994 = 0.207 \text{ (from Eq. F.8).}$$

e. Calculation of AC(UP), the Corrected Average Total UF₆ Production Rate at Any Value of F

The corrected average total UF₆ production rate, AC(UP), at any value of $F = n$ is the area under the corrected total UF₆ production rate curve to the time, T_n , when $F = n$.

$$AC(UP)_n = \frac{C(UP)_n}{T_n} \quad (F.10)$$

The time, T_n , when $F = n$ can be read directly from Fig. 13.

Example 7. Run 4. Time when $F = 0.5$, fluorine basis.

$$T_n = T_{0.5} = \frac{53.2}{60} \text{ min} = 0.887 \text{ hr (from Fig. 13).}$$

The area under the corrected total UF₆ production rate curve to $F = n$ (from Eq. F.8) is

$$F_n = \frac{C(UP)_n}{UA} \text{ or}$$

$$C(UP)_n = F_n(UA). \quad (F.11)$$

Substituting Eq. F.11 in Eq. F.10, we have

$$AC(UP)_n = \frac{F_n(UA)}{T_n}. \quad (F.12)$$

Example 8. Run 4. Average UF₆ production when $F = 0.5$, fluorine basis.

$UA = 12.25 \text{ lb (from Example 5);}$

$T_{0.5} = 0.887 \text{ hr (from Example 7);}$

$$A(UP)_{0.5} = \frac{0.5(12.25)}{0.887} = 6.91 \text{ lb/hr (from Eq. F.12).}$$

f. Corrections for Variations in the Partial Pressure of the BrF₅ Feed and in the Superficial Velocity

Two of the independent variables (partial pressure of the BrF₅ feed and fluidizing velocity) could not be controlled as precisely as the other variables (temperature, particle size, etc.). Corrections to bring

these effects to an average value were felt necessary to express more clearly the effect of the variables on the average total UF_6 production rates.

The average values of the partial pressure and gas velocity for the runs were:

	Partial Pressure of BrF_5 in Feed Gas, atm	Superficial Velocity of Feed Gas, ft/sec
Average High Value	0.289	0.829
Average Low Value	0.163	0.550

The differences between the BrF_5 partial pressure and gas velocity for each run and the corresponding averages were calculated.

Example 9. Run 4. BrF_5 partial-pressure correction.

BrF_5 partial pressure for Run 4	0.284 atm
Average high BrF_5 partial pressure	0.289 atm
Difference	+0.005 atm
Fluidizing-gas velocity for Run 4	0.53 ft/sec
Average low value of fluidizing-gas velocity	0.55 ft/sec
Difference	+0.02 ft/sec

The effect of BrF_5 partial pressure of the feed on UF_6 production rates is the difference between the average production rate of the runs with the higher partial pressure, HP_A , and those with the lower partial pressure, LP_A .

Example 10. Calculation of the uncorrected effect of partial pressure of BrF_5 feed on total UF_6 production rate.

Runs with the higher partial pressure: 4, 6, 7B, and 9.

Runs with the lower partial pressure: 5, 8, 10, and 11.

$$E_{pp} = \frac{(\text{Runs } 4+6+7B+9) - (\text{Runs } 5+8+10+11)}{4}, \text{ lb/hr } \text{UF}_6;$$

$$E_{pp} = \frac{(6.91 + 8.26 + 3.57 + 8.64) - (3.41 + 6.87 + 3.93 + 3.84)}{4}$$

$$= 2.33 \text{ lb/hr UF}_6$$

The correction for the variations in the partial pressure of the BrF_5 feed is its uncorrected effect, E_{pp} , on UF_6 production per atmosphere, times the difference between the BrF_5 partial pressure used in the run and the average BrF_5 partial pressure.

Example 11. Correction for deviation from average partial pressure.

Effect per atmosphere = $E_{pp} / (\text{average high} - \text{average low partial pressure})$

$E_{pp} = 2.33 \text{ lb/hr}$ (from Example 10);

Average high = 0.289 atm (Example 9);

Average low = 0.163 atm (above Example 9);

Effect per atmosphere = $\frac{2.33}{0.289 - 0.163} = 18.49 \text{ lb/hr/atm}$;

Difference between Run 4 value and average value = 0.005 atm (from Example 9).

Correction for variation in partial pressure = 18.49×0.005

= 0.092 lb/hr.

Corrected UF_6 production rate = $6.91 + 0.092 = 7.002 \text{ lb/hr}$.

All the runs are corrected for deviations from the average BrF_5 partial pressure in this manner and similarly for the variations in superficial velocity. After the corrections are made, the true effect of the variables can be determined as in Example 10.

2. Calculation of the Effects of the Independent Variables on the Average UF_6 Production Rate in the Fluid Bed Only

Calculation of the effect of the variables on the average UF_6 production rates, $A(\text{UP})$, in the fluid bed required the following steps:

- a) Calculation of the average UF_6 production rate in the fluid bed from the uranium analysis of the bed samples.

- b) Calculation of the average UF_6 production rate in the fluid bed to any value of F .
- c) Correction for variations in the values of the independent variables.
- a. Calculation of the Average UF_6 Production Rate in the Fluid Bed from the Uranium Analyses of the Bed Samples

The average UF_6 production rate in the fluid bed over a given time period, $A(\text{UP})_n$, can be calculated from the change in uranium concentration calculated from uranium analyses of bed samples taken at intervals. The procedure involves:

1) Determining the number of grams of uranium in the bed at the start of the time period.

$$(\text{Bed wt})_{i-1}(\text{w/o U})_{i-1} = \text{grams of uranium};$$

$$10301.4(0.2966) = 3056.3 \text{ g.}$$

2) Correcting the bed weight for the amount of uranium reacted and uranium removed in samples. Corrections are also made to adjust the data for the presence of UO_2F_2 and U_3O_8 in the bed according to the data of Anastasia et al.⁴

$$\text{New bed wt}_i = \text{Old bed wt}_i - \text{sample removed.}$$

$$\text{Old bed wt}_i = \text{New bed wt}_{i-1} \left(\frac{1 - \text{w/o U}_{i-1}(0.01223)}{1 - \text{w/o U}_i(0.1223)} \right),$$

where the constant 0.01223 accounts for the molecular weight of U_3O_8 and UO_2F_2 present at 300°C . At 225°C , the constant is 0.01201.

$$\text{New bed wt}_i = 10301.4 \frac{0.6373}{0.7126} - 70.6 = 9142.2.$$

The amount of uranium in the (old bed)_i is determined as in Step 1 and is subtracted from the amount obtained in Step 2 to obtain the uranium reacted over the time period. The UF_6 rate is then just this amount, converted to UF_6 and divided by the time interval.

$$\begin{aligned} A(\text{UP}) &= \frac{(\text{U in Bed}_i) - (\text{U in Bed}_{i-1})}{\text{Time Interval}} 0.1956 = \frac{3056.3 - 2132.2}{20} 0.1956 \\ &= 90.37 \text{ lb/hr.} \end{aligned}$$

The constant (0.1956) converts minutes to hours and uranium to UF_6 .

b. Calculation of the Average UF_6 Production Rate in the Fluid Bed to Any Value of F

The average UF_6 production rate in the fluid bed, $A(UP)_n$, to any value of F ($F = n$) is the total UF_6 produced, UP_n , to $F = n$ divided by the time, T_n , when $F = n$. (The data for the example are taken from Fig. 14.)

Fig. 14. Plot of UF_6 Production Rate in the Fluid Bed for Run 4

$$A(UP)_n = \frac{UP_n}{T_n} \text{ (from Eq. F.10).}$$

The time, T_n , when $F = n$ is taken as the average of the times for the fluorine- and bromine-based total UF_6 production rates so that the effects of the variables on the rates in the bed can be compared with the effects on the total rates. These times, T_n , can be read directly from the graphs (Fig. 13) of F for the fluorine and bromine basis (Fig. 12).

Example 12. Run 4. Time $T_{0.5}$ when $F = 0.5$.

$T_{0.5}$ fluorine basis = 53.2 min, bromine basis = 47.8 min (from Fig. 12).

$T_{0.5}$ fluid bed = average of bromine and fluorine basis =

$$\frac{53.2 + 47.8}{2} = \frac{50.5 \text{ min}}{60 \text{ min/hr}} = 0.841 \text{ hr.}$$

The total UF_6 produced, UP_n , to $F = n$ is the sum of the incremental areas under the UF_6 production rate curve to T_n (Fig. 14).

$$UP_n = \Delta A_1 + \Delta A_2 + \dots + \Delta A_n \text{ (Eq. F.2).}$$

The incremental area, ΔA_n , is the average UF_6 production rate of the area, aR_n , multiplied by the time increment of the area, Δt_n .

$$\Delta A_n = aR_n \times \Delta t_n \text{ (Eq. F.3).}$$

The average UF_6 production rate of the incremental area is obtained from Fig. 14, and the time increment is the difference between the time at the end and start of the incremental area.

$$\Delta t_n = t_{en} - t_{sn} \text{ (Eq. F.5).}$$

Substituting Eq. F.5 in Eq. F.3, we have

$$\Delta A_n = aR_n(t_{en} - t_{sn}). \quad (F.13)$$

Example 13. Run 4. Total UF_6 produced to $F = 0.5$.

$$UP_{0.5} = \Delta A_1 + \Delta A_2 + \dots + \Delta A_{0.5} \text{ (from Eq. F.2).}$$

From Eq. F.13,

$$\Delta A_1 = aR_1(t_{e1} - t_{s1}) = 9.04(1/3 - 0) = 3.01 \text{ lb,}$$

$$\Delta A_2 = aR_2(t_{e2} - t_{s2}) = 9.06(2/3 - 1/3) = 3.02 \text{ lb,}$$

$$\Delta A_{0.5} = aR_{0.5}(t_{e0.5} - t_{s0.5}) = 5.829(50.5/60 - 2/3) = 1.02 \text{ lb,}$$

and

$$UP_{0.5} = 3.01 + 3.02 + 1.02 = 7.05 \text{ lb.}$$

Example 14. Run 4. Average UF_6 production rate to $F = 0.5$.

$$A(UP)_{0.5} = \frac{UP_{0.5}}{T_{0.5}} \text{ (from Eq. 10);}$$

$$UP_{0.5} = 7.05 \text{ lb (from Example 13);}$$

$$T_{0.5} = 0.84 \text{ hr (from Example 12);}$$

$$A(UP)_{0.5} = \frac{7.05}{0.84} = 8.39 \text{ lb/hr.}$$

c. Correcting for Variations in Values of the Independent Variables

As described in Section 1.f of this appendix, corrections were necessary for those variables that could not be precisely controlled. The calculations for the average production rate in the fluid bed were similar to those for the average production rate of the entire system (Section 1.f of this appendix), with the average UF_6 production rates in the fluid bed substituted (in the equations) for the average UF_6 production rates in the entire system.

3. Calculation of the Effects of the Independent Variables on the Average UF_6 Production Rates "Elsewhere"

The " UF_6 produced elsewhere" is the difference between that produced in the fluid bed and the total production. Subtracting the effect of a variable on UF_6 production rate in the fluid bed from its effect on total UF_6 production rate yields its effect on " UF_6 production elsewhere."

4. Calculations of the Effects of the Independent Variables on BrF_5 Utilization

The effect of the independent variables on the average BrF_5 utilization efficiency was calculated at three values of F (0.5, 0.667, and 0.75) for (1) the total system and (2) the fluid bed only.

a. Calculation of the Effects of the Independent Variables on the Average Total BrF_5 Utilization of the System

Calculation of the effect of the independent variables on the average BrF_5 utilization of the total system from the fluorine and bromine analyses of the off-gas samples required the following steps:

- 1) Calculation of the instantaneous BrF_5 utilization.
- 2) Calculation of the average BrF_5 utilization to any desired F .
- 3) Corrections for variations in the BrF_5 partial pressure and in superficial velocity.
- 4) Calculation of the effects of the variables on the BrF_5 utilization.

(1) Calculation of the Instantaneous BrF_5 Utilization. The instantaneous BrF_5 utilization, (%), IU, for the total system from the fluorine and bromine content of the off-gas samples was calculated as follows:

Fluorine Basis

$$\text{Instantaneous BrF}_5 \text{ utilization, } IU = (U/F)(47.88)$$

where

U = uranium content (mg/ml) of the gas sample,

F = fluorine content (mg/ml) of the gas sample,

and

47.88 = conversion factor based on (1) the stoichiometry of the equation $U_3O_8 + 3.6BrF_5 \rightarrow 3UF_6 + 1.8Br_2 + 4O_2$ and (2) the units of measurement collected.

Bromine Basis

$$\text{Instantaneous BrF}_5 \text{ utilization, } IU, = (U/Br)(40.28),$$

where

U = uranium content (mg/ml) of the gas sample,

Br = bromine content (mg/ml) of the gas sample,

and

40.28 = conversion factor based on (1) the stoichiometry of the equation $U_3O_8 + 3.6BrF_5 \rightarrow 3UF_6 + 1.8Br_2 + 4O_2$ and (2) the units of conversion

The results of these calculations were averaged and plotted against time (see Fig. 15).

Fig. 15. Total BrF₅ Utilization, Average of Bromine and Fluorine Basis for Run 4

(2) Calculation of the Average BrF_5 Utilization to Any Desired F . The average total BrF_5 utilization, U , to any desired F ($F = n$) equals A_n , the area under the curve to $F = n$, divided by T_n , the time elapsed to $F = n$ (see Fig. 15).

$$U_n(\%) = \frac{A_n}{T_n}. \quad (\text{F.14})$$

The time, T_n , elapsed to $F = n$ equals the average of the times obtained on the bromine and fluorine bases to $F = n$. (Figure 14 shows the calculation to $F = 0.5$ for total UF_6 production.)

$$T_n = \frac{bt_n + ft_n}{2}, \quad (\text{F.15})$$

where

bt_n = time when $F = n$ for the bromine-based total UF_6 production,

and

ft_n = time when $F = n$ for the fluorine-based total UF_6 production.

Example 15. $F = 0.5$, Run 4.

From Fig. 13,

$bt_{0.5} = 47.8$ min, and $ft_{0.5} = 53.2$ min.

$$\text{Then } T_{0.5} = \frac{bt_{0.5} + ft_{0.5}}{2} = 50.5 \text{ min.}$$

The area under the curve, A , to $F = n$ equals the sum of the incremental areas to $F = n$.

$$A_n = \Delta A_1 + \Delta A_2 + \dots + \Delta A_n \text{ (Fig. 15)}. \quad (\text{F.16})$$

An incremental area equals the average utilization of the area, AU , multiplied by the time increment, Δt , of the area.

$$\Delta A_n = AU_n \times \Delta t_n. \quad (\text{F.17})$$

The average utilization of the area, AU , is the average of the instantaneous utilizations at the start, IU_S , and end, IU_E , of the incremental area.

$$AU_n = \frac{IU_S + IU_E}{2} \quad (F.18)$$

The time increment, Δt , is the difference between the time at the end, t_E , and at the start, t_S , of the area.

$$\Delta t_n = t_E - t_S \quad (F.19)$$

Substituting Eqs. F.18 and F.19 in Eq. F.17, we have

$$\Delta A_n = \frac{IU_S + IU_E}{2} (t_E - t_S) \quad (F.20)$$

For the first incremental area, the instantaneous utilization at the start is unknown. Therefore the average utilization, AU_1 , was assumed to be the same as the instantaneous utilization at the end, IU_{E1} . Equation F.18 for the first incremental area reduces to

$$AU_1 = IU_{E1}$$

and Eq. F.20 becomes

$$\Delta A_1 = IU_{E1} (t_{E1} - t_{S1})$$

Example 16. Run 4. Average BrF_5 utilization, first incremental area.

From Fig. 15,

$$IU_{E1} = 82.59\%, \quad t_{E1} = 20 \text{ min}, \text{ and } t_{S1} = 0 \text{ min.}$$

Then,

$$\Delta A_1 = (82.59)(20 - 0) = 1651.7\% \text{-min.}$$

For the incremental area in which $F = n$, the instantaneous utilization at the end, IU_{En} , is not known. The instantaneous utilization at this point is a distance along the curve proportional to the fraction of the total time of the area containing the point when $F = n$.

$$IU_{En} = IU_{Sn} - (IU_{Sn} - IU_{Sn+1}) \frac{t_n - t_{Sn}}{t_{Sn+1} - t_{Sn}} \quad (F.21)$$

Example 17. Run 4. Instantaneous utilization at $F = 0.5$.

From Fig. 15,

$IU_{Sn} = 67.10\%$, $IU_{Sn+1} = 52.84\%$, $t_n = 50.5$ min, $t_{Sn} = 40$ min,
and $t_{Sn+1} = 60$ min.

$$\text{Then } IU_{En} = 67.10 - (67.10 - 52.84) \frac{50.5 - 40}{60 - 40} = 59.61\%.$$

Substituting values from Fig. 14 and Example 16 into Eq. F.20, we have

$$\Delta A_{0.5} = \frac{67.10 + 59.61}{2} (50.5 - 40) = 655.23\%-\text{min}.$$

For Run 4, it remains only to calculate the incremental area, ΔA_2 . The calculation for this is straightforward from Eq. F.20.

Example 18. Run 4. Second incremental area.

$$\Delta A_2 = \frac{IU_{S_2} + IU_{E_2}}{2} (t_{E_2} - t_{S_2}).$$

From Fig. 15,

$$IU_{S_2} = 82.58, IU_{E_2} = 67.10, t_{E_2} = 60, t_{S_2} = 40,$$

and

$$\Delta A_2 = \frac{82.58 + 67.10}{2} (60 - 40) = 1496.80\%-\text{min}.$$

This completes all the data required to calculate the area under the curve and the average total BrF_5 utilization to $F = 0.5$ for Run 4.

Example 19. Run 4. Average total BrF_5 utilization at $F = 0.5$.

From Example 16, $\Delta A_1 = 1651.7\%-\text{min}$;

From Example 18, $\Delta A_2 = 1496.80\%-\text{min}$;

From Example 17, $\Delta A_{0.5} = 655.23\%-\text{min}$.

$$A_{0.5} = 1651.7 + 1496.80 + 655.23 = 3803.7 \text{ (from Eq. F.16).}$$

From Example 16, $T_{0.5} = 50.5$ min;

$$U_{0.5} = \frac{3803.7}{50.5} = 75.32 \text{ (from Eq. F.14).}$$

(3) Corrections for Variations in the BrF_5 Partial Pressure and in Superficial Gas Velocity. Corrections of the average total BrF_5 utilization for variations in the partial pressure of the BrF_5 feed and the fluidizing-gas velocity are similar to corrections made on the UF_6 production rates (see Section 1.f of this appendix).

(4) Calculation of the Effects of the Variables on the BrF_5 Utilization. Calculation of the effects of the independent variables on the average total BrF_5 utilization is similar to calculations of the UF_6 production rates (see Section 1.f of this appendix).

b. Calculation of the Effects of the Independent Variables on the Average BrF_5 Utilization in the Fluid Bed Only

Calculation of the effect of the variables on the average BrF_5 utilization in the fluid bed required the following steps:

- 1) Calculation and plotting of the average BrF_5 utilization between bed samples.
- 2) Calculation of the average BrF_5 utilization to a given value of F .
- 3) Correction for variations in the BrF_5 partial pressure of the feed and for variations in the fluidizing velocity.
- 4) Calculation of the effects of the independent variables on BrF_5 utilization.

(1) Calculation of the Average Utilization between Bed Samples. The average BrF_5 utilization can be obtained by first calculating the theoretical maximum UF_6 production rate from the average BrF_5 feed rate and the stoichiometry of the reaction.

$$\text{Max } \text{UF}_6 \text{ rate} = \text{Average } \text{BrF}_5 \text{ feed rate (1.6775)} = 7.53 \text{ (1.6775)};$$

$$\text{Max } \text{UF}_6 \text{ rate} = 12.64 \text{ lb/hr.}$$

The average BrF_5 utilization efficiency is then

$$\text{AU, Average } \text{BrF}_5 \text{ Utilization} = \frac{\text{Actual } \text{UF}_6 \text{ rate}}{\text{Theor. max } \text{UF}_6 \text{ rate}} \cdot 100 = \frac{1.212}{12.64} \cdot 100;$$

$$\text{AU, Average } \text{BrF}_5 \text{ Utilization} = 9.63\%.$$

The values obtained for Run 4 are plotted against time in Fig. 16.

(2) Calculation of the Average BrF_5 Utilization in the Fluid Bed to F . The average BrF_5 utilization in the fluid bed, U , to any desired F ($F = n$) equals A , the area under the curve to $F = n$, divided by T , the time elapsed to $F = n$ (see Fig. 16).

Fig. 16. BrF_5 Utilization in the Fluid Bed for Run 4

$$U_{Fn}(\%) = \frac{A_{Fn}}{T_{Fn}} \quad (\text{F.22})$$

The time elapsed to T_{Fn} for the total BrF_5 utilization (Eq. F.15) is used as the T_{Fn} for BrF_5 utilization in the bed so that they are on the same basis.

Example 20. Run 4, when $F = 0.5$.

Since T_{Fn} for the fluid-bed BrF_5 utilization is taken as being equal to T_{Fn} for the total utilization from Example 15,

$$T_{F0.5} = 50.5 \text{ min.}$$

As shown in Eqs. F.16 and F.17, the area, A_n , under the curve to $F = n$ is

$$A_{Fn} = \Delta A_1 + \Delta A_2 + \dots + \Delta A_{Fn} \text{ (Fig. 16).} \quad (\text{F.23})$$

The incremental areas are

$$\Delta A_n = aU_n \times \Delta t_n \text{ (from Eq. F.3).} \quad (\text{F.24})$$

The average utilization of an incremental area, aU_n , is obtained directly from Fig. 16, and the time increment is the difference between the time at the end and the time at the start of the area (Eq. F.19).

$$\Delta t_n = t_{En} - t_{Sn}. \quad (\text{F.25})$$

Substituting Eq. F.25 in Eq. F.24 produces

$$\Delta A_n = aU_n(t_{En} - t_{Sn}). \quad (\text{F.26})$$

Example 21. Run 4, when $F = 0.5$.

From Example 20, $T_{F0.5} = 50.5$ min.

From Fig. 16,

$$aU_1 = 94.33\%, \quad aU_2 = 94.54\%, \quad aU_{F0.5} = 48.33\%;$$

$$t_{S1} = 0 \text{ min}, \quad t_{E1} = t_{S2} = 20 \text{ min}, \quad t_{E2} = t_{SF0.5} = 40 \text{ min};$$

$$t_{EF0.5} = 50.5 \text{ min.}$$

$$\text{From Eq. F.26, } \Delta A_1 = aU_1(t_{E1} - t_{S1}) = 94.33(20 - 0) = 1866.6\%-\text{min};$$

$$\Delta A_2 = aU_2(t_{E2} - t_{S2}) = 94.54(40 - 20) = 1890.8\%-\text{min};$$

$$\begin{aligned} \Delta A_{F0.5} &= aU_{F0.5}(t_{EF0.5} - t_{SF0.5}) = 48.33(50.5 - 40) \\ &= 507.5\%-\text{min.} \end{aligned}$$

$$\begin{aligned} \text{From Eq. F.23, } A_{F0.5} &= \Delta A_1 + \Delta A_2 + \Delta A_{F0.5} = 1866.6 + 1890.8 \\ &+ 507.5 = 4284.9\%-\text{min.} \end{aligned}$$

$$\text{From Eq. F.22, } U_{F0.5} = \frac{A_{F0.5}}{T_{F0.5}} = \frac{4284.9}{50.5} = 84.85.$$

(3) Correction for Variations in BrF_5 Partial Pressure in the Feed and for Variations in the Fluidizing Gas Velocity. These corrections are similar to those made on the UF_6 production rates (Section 1.f of this appendix).

(4) Calculation of the Effects of the Independent Variables on the Average BrF_5 Utilization in the Fluid Bed Only. The calculations are similar to those made on the UF_6 production rates (Section 1.f of this appendix).

5. Calculations of the Effects of the Independent Variables on the Diminishing-sphere Rate Constants, k , for the BrF_5 - U_3O_8 Reaction

The diminishing-sphere rate constant, k , is the slope of the curve $(1 - F)^{1/3}$ plotted against time. Since F is known from the calculations made on the total UF_6 production rates, it remains only to calculate and plot $(1 - F)^{1/3}$ (as in Fig. 17 for Run 4). The slope, k , is $Y \div X$ taken from the graph, and the effects of the independent variables on k are calculated as in Section 1.f of this appendix with appropriate corrections for variations in the superficial gas velocity and BrF_5 partial pressure.

Fig. 17. Determination of Diminishing-sphere Rate Constant for Run 4

6. Calculation of Experimental Error

The experimental error can be estimated for this series of experiments by using the effect of the "error" variables and the results of any duplicated runs, as described in Sections III (Operating Conditions) and IV.A.3 (Homogeneity of the Fluid Bed). An example of this calculation for the total UF_6 production rate to $F = 0.5$, calculated from bed samples, follows.

The variance for effects is given by

$$V_{\text{eff}} = \frac{\sum_{1}^n E_{\text{Error}}^2 + \sum_{1}^m \frac{1}{2}(Y_a - Y_b)^2}{n + m}$$

Using the data from Tables XI and XII,

$$E_{\text{Error}} = 0.809,$$

$$Y_3 - Y_4 = 1.458,$$

$$n = 1, m = 1, n + m = 2,$$

gives

$$V_{\text{eff}} = 0.783,$$

and

$$SE_{\text{eff}} = \sqrt{V_{\text{eff}}} = 0.885.$$

The t_i 's can be calculated as follows:

$$t_i = \frac{E_i}{SE},$$

$$t_T = 2.378,$$

$$t_{P.P.} = 3.431,$$

$$t_{Vel} = 1.176,$$

$$t_{Chg} = 1.884,$$

$$t_d = 1.479,$$

and

$$t_{F.P.} = 0.676.$$

The calculated t_i can be tested against values of t with $n + m = 2$ degrees of freedom. Application of this test shows that the effect of BrF_5 partial pressure is statistically significant at the 90% confidence level and that the effects of temperature and charge are significant at the 80% confidence level. All other effects are not statistically significant. If one assumes that there is no effect of the presence of fission products and uses its calculated effect as an error estimator, the variance and standard error become

$$V_{\text{eff}} = 0.641, \text{ and } SE_{\text{eff}} = 0.801.$$

This estimate of the standard error (three degrees of freedom) can be used in the t test to give the following t_i 's:

	<u>Significant at</u>		<u>Significant at</u>
$t_T = 2.628$	90%	$t_{Chg} = 2.082$	80%
$t_{P.P.} = 3.792$	95%	$t_d = 1.635$	80%
$t_{Vel} = 1.299$	-		

This better estimate of the standard error shows that there may also be a significant effect of the size of the UO_2 charge. This was not revealed in the other test.

Addition of the estimated individual variances involved in calculating the UF_6 production rate gave the variance of an effect as

$$V_{\text{eff}} = 0.55 \text{ and } SE_{\text{eff}} = 0.75,$$

which compares well with the estimate made from the "error" effects and duplicate runs. This error analysis revealed that the major source of error is a combined sampling and analytical error involved in obtaining the uranium concentration in the bed.

In summary, the standard error for the UF_6 production rate, at $F = 0.5$, from bed samples is about 0.8. This means that the calculated effects have a precision of about ± 1.6 lb/hr at the 95% confidence level. The measured results (UF_6 production rates) have a precision of about ± 3.2 lb/hr at the 95% confidence level.

APPENDIX G

Uranium Retention in Traps

The percent of the uranium charged which was retained as UF_6 on the first two NaF traps is given in Table XXII. These traps were operated at about 150°C and contained about 18 kg of NaF pellets. The effects of the variables (in the fluid-bed reactor) on the trapping efficiency are also presented. Since the standard error for an effect is about 7.6 (estimated from E_{Error} and by comparing Runs 7A and 7B with Runs 3 and 4), the only statistically significant (at 90% confidence level) effect is that of the size of the UO_2 charge. This effect means that when 4.4 kg of UO_2 was used, the capacity of the first two traps was exceeded. The average retention for the runs with 4.4-kg UO_2 charges was 0.214 kg of UF_6 per kg of NaF. This value agrees quite well with data obtained on trapping UF_6 from a fluorine-nitrogen stream in prototype equipment at ORGDP.⁵⁴

TABLE XXII. Efficiency of Sodium Fluoride Trap

Run	Percentage of Uranium Charged Found in NaF Traps 1 and 2
3	87.10
4	65.43
5	94.94
6	98.40
7A	90.39
7B	87.27
8	52.40
9	52.88
10	92.57
11	93.69

Variable	Effect of (+) Levels of Variables on Percentage of Charge Trapped
E_T = Temperature of fluid bed	-4.43
$E_{P.P.}$ = Partial pressure of BrF_5	-8.65
E_{Vcl} = Gas velocity in fluid bed	-11.27
E_{Chg} = Charge of UO_2	-26.57
E_d = Particle size of alumina	-16.27
$E_{F.P.}$ = Fission products	7.11
E_{Error} = Error	10.56

APPENDIX H

Material Balances

As shown by Table XXIII, the total uranium accounted for was $100 \pm 5\%$ of that charged (5% is the estimated analysis accuracy) for seven of the ten runs made. In the runs with good material balances, the sodium fluoride traps consistently contained more than 90% of the uranium charged (90.39 to 98.45%); in the runs with poor material balances, the traps consistently contained less than 90% of the uranium charged (67.27 to 87.36%). As the percentage of the charge found in the traps decreased, the total uranium accounted for decreased, as shown in the following tabulation, indicating that losses through the traps or poor sampling techniques caused the poorer material balances:

Run No.	Percentage of Uranium Charged	
	In Traps	Accounted For
7B	87.36	91.44
8	72.43	81.26
9	62.27	65.36

Sampling errors were checked as follows: New samples were obtained from two of the traps by resplitting all the sodium fluoride, and four of the original samples were redissolved and reanalyzed. Only one of the original samples changed more than the estimated $\pm 5\%$ analytical error, and the average change of -1.61% was well within the estimated accuracy. This indicated that the samples were homogeneous and that the analytical errors would have small effects on the total material balance. The uranium analyses of the new samples differed from the uranium analyses of the original samples by more than the estimated analytical error, but the difference could account for only a small part of the uranium not previously accounted for, as shown in Table XXIV.

Downstream from the traps, the off-gas passed through a scrubbing system. Precipitated uranium was found on the filters of the system after each run, indicating that the NaF traps had not removed all the UF_6 product. After the scrub-liquid collection tank was drained, uranium solids that had not been included in the material balance were found at the tank bottom. This is probably part of the uranium not accounted for in the runs in which the material balance was low.

TABLE XXIII. Uranium Material Balances

	Run 3		Run 4		Run 5		Run 6		Run 7A		Run 7B		Run 8		Run 9		Run 10		Run 11	
	g	%	g	%	g	%	g	%	g	%	g	%	g	%	g	%	g	%	g	%
Uranium Charged	3837.0	100.0	3837.0	100.0	3837.0	100.0	1918.0	100.0	1918.0	100.0	1918.0	100.0	3837.0	100.0	3837.0	100.0	1918.0	100.0	1918.0	100.0
Uranium Recovered																				
NaF Traps	3530.0	92.01	3609.0	94.07	3662.0	95.45	1888.0	98.45	1734.0	90.39	1675.0	87.36	2779.0	72.43	2389.0	62.27	1809.0	94.32	1797.0	93.70
Bed Samples (O ₂ Step)	96.0	2.50	42.8	1.11	32.6	0.85	32.9	1.71	19.4	1.01	21.7	1.13	24.2	0.63	22.8	0.60	40.7	2.12	17.5	0.91
Bed Samples (BrF ₅ Step)	34.7	0.90	36.9	0.96	42.0	1.09	18.0	0.94	14.6	0.76	27.3	1.42	20.0	0.52	31.8	0.83	47.7	2.49	15.1	0.78
Off-gas Samples	9.0	0.23	8.0	0.21	3.9	0.10	2.4	0.13	3.4	0.18	2.9	0.15	3.7	0.10	6.0	0.16	2.4	0.13	5.4	0.28
Scrubber Filters	67.0	1.75	8.8	0.23	2.4	0.06	3.9	0.20	5.5	0.29	2.1	0.11	5.2	0.14	51.5	1.34	18.0	0.92	8.9	0.46
TOTAL	3737	97.39	3706	96.58	3743	97.55	1945	101.43	1777	92.63	1729	90.17	2832	73.82	2501	65.20	1918	99.99	1844	96.14
Uranium Lost																				
Final Alumina Bed	2.6	0.07	0.7	0.02	26.8	0.70	5.3	0.28	16.7	0.87	5.9	0.31	17.0	0.44	3.9	0.10	3.4	0.18	1.4	0.07
Support Bed	0.7	0.02	3.3	0.09	3.9	0.10	1.8	0.09	7.6	0.40	4.5	0.23	6.2	0.16	0.6	0.02	0.2	0.01	15.8	0.82
Holdup	1.3	0.03	0.04	0	6.9	0.18	3.7	0.19	23.1	1.21	14.1	0.76	262.0	6.84	1.9	0.05	2.4	0.12	15.3	0.80
TOTAL	4.6	0.12	4.1	0.11	37.6	0.98	10.8	0.56	47.4	2.48	24.5	1.30	285.2	7.44	6.4	0.17	6.0	0.31	32.5	1.69
Accounted For	3741	97.51	3710	96.69	3781	98.54	1956	102.00	1824	95.10	1754	91.44	3118	81.26	2508	65.36	1924	100.30	1876	97.84
Gain or (Loss)	(95.4)	(2.49)	(127.0)	(3.31)	(56.1)	(1.46)	38.3	2.00	(93.9)	(4.90)	(164.0)	(8.56)	(719.0)	(18.74)	(1329.0)	(34.65)	5.9	0.30	(41.5)	(2.16)

TABLE XXIV. Variations due to Sampling and Analytical Errors for the Sodium Fluoride Traps

Run No.	Trap No.	Percentage of Uranium Charged		Change, %
		Original Sample	Redissolution	
7B	1	12.90	13.00	+0.77
7B	2	1.92	1.81	-6.07
8	2	8.90	9.22	+3.59
9	2	9.40	9.10	-3.19
Average				-1.61

Run No.	Trap No.	Percentage of Uranium Charged		Change, %
		Original Sample	New Sample	
9	1	9.8	9.2	-6.12
9	2	9.25 ^a	8.9	-3.93
Average				-5.04

^aAverage analysis of original sample and redissolved sample.

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