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ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

*Part 3. Fluid-bed Fluorination of
Uranium Dioxide Fuel Pellets*

by

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	9
I. INTRODUCTION.	10
II. EQUIPMENT AND PROCEDURE.	12
A. Fluid-bed System.	12
B. Special Equipment	13
1. Fluorine Supply	14
2. Fluorine Analysis.	14
a. Batch Samples	14
b. Continuous Analysis	16
3. Automatic Temperature Control of the Reactor	18
4. Pellet Charger.	20
C. Procedure.	20
III. RESULTS AND DISCUSSION.	22
A. Preliminary Fluorination Experiments.	22
1. Effect of Fluorine Concentration.	23
2. Effect of Pellet-bed Height.	23
3. Production of Intermediate Fines of Uranium Fluoride	24
4. Effect of Height of Fluidized Bed.	26
5. Kinetics of the Reaction.	26
6. Operational Experience.	27
7. Effect of Operational Parameters on the Process for the Direct Fluorination of UO_2	28
B. Effect of Conditions of Pellet Manufacture on the Fluorination Reaction	28
C. Effect of Fluid-bed Material.	30
D. Effect of Fluid-bed Height	32
E. Fluorination of Uranium Dioxide Pellets.	32
1. Gas-solid Reactions, Direct Fluorination	32
2. Steady-state Effects of Gas Velocity on Fluorination Rates	33
3. Fluorination of UO_2 Pellets without a Fluid Bed.	34
4. Effect of Oxygen on Batch Fluorination of UO_2 Pellets.	35
5. Effect of Temperature on Fluorination Rates with Oxygen and Nitrogen Dilution of Fluorine	38
6. Effect of Oxygen on the Fluorination at Steady- state Conditions	39

TABLE OF CONTENTS

	<u>Page</u>
F. Oxidation of Uranium Dioxide Pellets	40
1. Fluorination of Oxidized Pellets	42
G. Removal of UO_2 Pellets from Cladding Materials	43
1. Chemical Decladding of Simulated Fuel Rods Clad in Zircaloy-2	44
2. Removal of UO_2 from Mechanically Broached 304 Stainless Steel	45
a. Short Lengths of Simulated, Chopped Fuel Rods . .	45
b. Simulated Fuel-rod Bundles	51
H. Fluorination of Deep Beds of UO_2 Pellets	54
1. Operating Conditions	55
2. Single-pass Gas Flow--Runs 50 and 52	56
3. Recycled Gas--Runs 49, 53, 54, and 55	58
4. Summary Evaluation of Deep-bed Runs	62
I. Two-zone Oxidation-Fluorination of UO_2 Pellets	63
1. Gas-Solid Chemical Reactions	63
2. Control of Fines Transport from the Oxidation Zone . .	64
3. Effect of Reactant Gas Concentration	69
4. Production Rates and Fluorine Utilization for the Batch Processing of UO_2 Pellets	71
IV. CONCLUSIONS	72
V. ACKNOWLEDGMENTS	75
VI. BIBLIOGRAPHY	76
VII. APPENDIX A. Mathematical Analysis of a Gas Recycle Applied to the Fluorination of UO_2 Pellets	78

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Conceptual Flowsheet for Fluidized-bed Fluoride Volatility Process	11
2.	Schematic Diagram of Equipment for Fluorination of Uranium Dioxide Pellets	12
3.	High-pressure Fluorine Manifold and Supply System.	14
4.	Schematic Diagram of Fluorine Analyzer Assembly	15
5.	Schematic Diagram of Fluorine Analyzer System.	16
6.	Continuous Fluorine Analysis of Fluorinator Effluent Gas by Thermal Conductivity Methods	17
7.	Fluorine Flow Control System for Temperature Control in Uranium Dioxide Pellet Fluorinations	18
8.	Column Temperatures during Run 29.	19
9.	Uranium Dioxide Pellet Charger.	20
10.	Operational Methods for the Fluorination of Uranium Dioxide Pellets	21
11.	Fluid-bed Reactor for Preliminary Studies of the Fluorination of Uranium Dioxide Pellets.	22
12.	Uranium Hexafluoride Production and Fluorine Utilization as a Function of Inlet Fluorine Concentration	23
13.	Uranium Hexafluoride Production and Fluorine Utilization as a Function of Pellet-bed Height.	24
14.	Particle-size Distribution of Norton Alundum Mixtures Used in Uranium Dioxide Pellet Fluorination Runs.	31
15.	Fines Concentration in Fluidized Bed, Runs 31, 32, and 34. . .	37
16.	Fluorine Inlet Concentration and Fluorine Utilization for Run 32.	37
17.	Fluorine Inlet Concentration and Fluorine Utilization for Run 34.	37
18.	Fluid-bed Fluorination of Uranium Dioxide Pellets: Temperature Dependence.	39
19.	Schematic Diagram of Closed-loop System for Batch Oxidation of Uranium Dioxide Pellets.	41
20.	Particle-size Distribution of U_3O_8 Fines, Run 45	42

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
21.	Typical Specimens of Type 304 Stainless Steel-clad Uranium Dioxide Fuel Segments	47
22.	Appearance of Typical Stainless Steel-cladding Residues from Run 71	47
23.	Uranium Dioxide Pellet Residues with Cladding Removed, Run 72	48
24.	Cladding Tubes Ruptured by the Oxidation of UO_2 to U_3O_8 during Run 76	52
25.	Uranium Hexafluoride Production Rates in Run 76	54
26.	Uranium Hexafluoride Production Rates in Run 52	57
27.	Comparison of Uranium Hexafluoride Production in Two Deep-bed Uranium Dioxide Pellet-fluorination Runs	58
28.	Uranium Hexafluoride Production during Run 53	60
29.	Average Nitrogen and Fluorine Feed Rates and Uranium Hexafluoride Production Rates, Run 53.	61
30.	Schematic Diagram of Two-zone Oxidation-Fluorination of Uranium Dioxide Pellets	64
31.	Bed Temperatures during Run 63	67
32.	Fluorine Feed Rates and Uranium Hexafluoride Production Rates for Run 69	69
33.	Fluorine Feed Rates and Uranium Hexafluoride Production Rates for Run 70	70
34.	Material Flow Diagram for Recycle Systems.	79

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Summary of Operating Conditions for Preliminary Fluorination Runs.	22
2.	Effect of Pellet-bed Height on Fluorine Utilization.	24
3.	Screen Analysis of Fines Produced during Fluorination of Uranium Dioxide Pellets--Run 11	25
4.	Effect of Operational Parameters on the Process for the Direct Fluorination of UO_2 Pellets.	28
5.	Prior History and Properties of Pellets Used in Fluorination Runs.	29
6.	Effect of Prior History on the Fluorination of UO_2 Pellets.	29
7.	Spectrographic Analysis of Norton's Alundum	31
8.	Effect of Gas Velocity upon Uranium Hexafluoride Production under Approximately Steady-state Conditions	33
9.	Effect of Oxygen on the Fluorination of UO_2 Pellets	36
10.	Uranium Hexafluoride Production Rates as a Function of Temperature and Fluorine Diluent.	38
11.	Effect of Oxygen on Uranium Hexafluoride Production Rates under Steady-state Conditions.	40
12.	Oxidation of Uranium Dioxide Pellets.	41
13.	Decladding of UO_2 Pellets in Zircaloy-2 Tubing.	44
14.	Operating Conditions for Fluid-bed Oxidation-Fluorinations with Short Segments of Simulated Fuel Rods	46
15.	Uranium Dioxide Distribution in Stainless Steel-clad Fuel Segments after Two-zone Oxidation-Fluorination, Run 75	49
16.	Results of Fluid-bed Oxidation-Fluorination Experiments with 0.94-in. Segments of Simulated UO_2 Fuel Rods Clad in Stainless Steel	50

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
17.	Operating Conditions for Fluid-bed Oxidation-Fluorination Experiments with Simulated Fuel Rods Which Were Mechanically Slit or Perforated	53
18.	Nominal Fluorination Conditions for Deep Beds of UO_2 Pellets	55
19.	Summary of Stable Operating Periods during Fluorination of 18-in. Uranium Dioxide Pellet Beds	59
20.	Summary Evaluation of Six Deep-bed Fluorination Runs	62
21.	Two-zone Oxidation-Fluorination of UO_2 Pellets	65
22.	Effect of Oxygen Concentration on Rate of UF_6 Production during Two-zone Oxidation-Fluorination.	69
23.	Operating Conditions and Results for Run 70	70
24.	Calculated Gain in Fluorine Efficiency for Typical Cases of Gas Recycle Operation	81

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by

L. J. Anastasia, J. D. Gabor,
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SUMMARY

Fluorination of ceramic fuel to volatile UF_6 and PuF_6 is a major step in a fluidized-bed fluoride volatility process for the recovery of uranium and plutonium from spent power reactor fuel. The fluorination of nonirradiated UO_2 pellets in a 3-in.-dia fluidized-packed bed reactor system has been carried out to demonstrate the fluorination step on a pilot-plant scale. The packed bed was formed by a batch of cylindrical pellets which were too large to fluidize directly. An inert fluidized medium was provided in the voids of the pellet bed and in the space above the bed to aid in heat removal for the highly exothermic reactions involved. Additional cooling capacity was provided by passing a stream of air past external fins attached to the reactor.

The experimental effects of most interest were the production rates for UF_6 , the efficiency of fluorine utilization, and the control of the reaction temperature. The fluorination was shown to proceed through an induction period of UO_2F_2 formation followed by a reaction period of high UF_6 production and high fluorine utilization. The presence of oxygen enhanced the fluorination by formation of U_3O_8 fines of high specific surface area and high reactivity. The temperature coefficient (E') for reaction with fluorine diluted with either oxygen or nitrogen was 14 kcal/g-mole UO_2 .

Application of fluidized-bed techniques to the dejacketing of clad, simulated fuel elements was investigated. The reaction of Zircaloy-2 cladding with a gas mixture consisting of HF-10% HCl, followed by in situ fluorination of the pellets, was shown to be more effective than direct fluorination of the clad specimens. For specimens clad in 304 stainless steel, oxidative removal of the UO_2 combined with fluorination of the oxidation product (U_3O_8) in a single vessel was studied. With fuel specimens 10 and 12 in. long, the UO_2 was effectively removed from cladding which had been mechanically slit or perforated. Complete UO_2 removal was obtained without the need for fluorination of the stainless steel and without the need for mechanical vibration of the cladding.

Relatively deep pellet beds of 18 in. (29 lb) could be processed at average production rates of 25 lb UF_6 /(hr)(sq ft reactor cross-sectional area) and good quality fluidization, but with low fluorine utilization of approximately 40%. Fluorine utilization of 75% was obtained by recycle of the process effluent gas; however, fluidization quality was poor when production rates averaged more than 20 lb UF_6 /(hr)(sq ft). With 12-in.-deep beds of pellets (20 lb) the highly exothermic fluorination reaction was carried out in a system which consisted of two reaction zones: one for the oxidation of the UO_2 pellets to U_3O_8 fines and one for the fluorination of U_3O_8 to UF_6 . In the two-zone system, the less-exothermic oxidation takes place in the fluidized-packed bed and the fluorination reaction takes place in a super-incumbent fluidized bed where heat transfer coefficients are higher than those in the fluidized-packed bed. With pulsation of the fluidizing gas, the 20-lb batches of UO_2 pellets were processed in about 12 hr at 500°C. Average production rates of 50 lb UF_6 /(hr)(sq ft) and fluorine utilization of 75% were demonstrated without the need for recycled gas and under conditions of good fluidization quality.

I. INTRODUCTION

Fluidized-bed fluoride volatility processes for the recovery of fissionable values from spent nuclear reactor fuels are under development at Argonne National Laboratory. Development studies are being made on the application of volatility techniques to the reprocessing of low-enrichment uranium dioxide ceramic fuels commonly used in central station power reactors and the high-enrichment fuels of the types used in mobile power reactors, test reactors, seed and blanket reactors, and others.¹

Central station power reactor fuels, generally of low enrichment with less than 5% U^{235} , are compressed to high-density pellets and contained in thin metal tubes of stainless steel or Zircaloy. The spent fuel contains plutonium which must also be recovered with the uranium. A conceptual flowsheet for the recovery of fissionable values from this type of fuel is shown in Fig. 1. The major steps in the process are: (1) separation of the fuel from the cladding, (2) reaction of the exposed fuel with elemental fluorine at elevated temperatures to form gaseous uranium and plutonium hexafluoride, (3) distillation to remove fission products, as well as to separate the hexafluorides into uranium hexafluoride and an enriched plutonium hexafluoride mixture with uranium hexafluoride, (4) separation of plutonium and uranium in the mixture by thermal decomposition of plutonium hexafluoride.

This report concerns a study of the pilot-plant development of the fluorination step in the flowsheet. In this study, nonirradiated uranium dioxide pellets were fluorinated in a fluidized-packed-bed reactor system. The packed bed was formed from a batch of cylindrical uranium dioxide pellets which were too large to fluidize directly. An inert fluidized medium was provided in the voids of the pellet bed and in the space above the bed to aid in heat removal for the highly exothermic reactions involved.

108-7606

Fig. 1. Conceptual Flowsheet for Fluidized-bed Fluoride Volatility Process

The experimental program was directed toward the batch fluorination of UO₂ pellets in a single vessel with primary interests being: (1) the batch-processing time, (2) the efficiency of fluorine utilization, and (3) the control of reaction temperatures.

The batch-processing time was dependent upon the rate of production for UF₆; in this respect, the desired experimental objective was to establish production rates of ~50 lb UF₆/(hr)(sq ft). An overall fluorine utilization efficiency of 75% was considered to be economically feasible for the full-scale process and, therefore, 75% fluorine utilization was also an experimental objective. As a third experimental objective, the rapid rates of production at high fluorine efficiencies were to be obtained at controlled reaction temperatures. This objective required that good fluidization quality be maintained throughout the batch-processing cycle. The quality of fluidization was monitored principally by temperature and pressure-drop measurements. Uniform temperatures and normal pressure drops in the reactor were indicative of good fluidization quality and, therefore, of good heat transfer.

II. EQUIPMENT AND PROCEDURE

A. Fluid-bed System

The arrangement of the experimental equipment is shown in Fig. 2. The fluidized-bed reactor was fabricated from a 3-in.-ID by $4\frac{1}{2}$ -ft-long nickel pipe; an 11-in.-ID disengaging section, 26 in. long, surmounted the fluid bed section of the reactor and housed the two process filters. The filters, 3 in. wide and 18 in. long, were composed of sintered nickel with a nominal porosity of $10\ \mu$. Automatic, periodic blowback of the filters was provided by means of reverse flow of nitrogen through nickel jets located immediately downstream of each filter. Filter blowback by a $1/2$ -sec burst of 30-psig nitrogen effectively removed solids caked on the filter and returned them to the reaction zone. Filter blowback by a

108-7138

Fig. 2. Schematic Diagram of Equipment for Fluorination of Uranium Dioxide Pellets

The reactor was heated by electric tubular heaters bonded to the reactor wall by a copper metallizing technique. The heaters were arranged longitudinally to provide separate 3-kW inputs to the lower and upper halves of the reactor. An additional 4.5 kW was provided by 6 strip heaters attached to the cooling fins. The heating system was modified for the two-zone oxidation-fluorination experiments to provide 6-kW input to the fluorination zone of the reactor and 3-kW input to the oxidation zone.

Twelve longitudinal fins, 3 in. wide, were attached around the circumference of the 3-in. section of the reactor. An annulus was formed by a metal

jacket and insulation around the fins. Cooling of the reactor could be provided by air passed through the annulus by a blower at a maximum rate of 400 cfm.

Uranium hexafluoride was collected in coiled copper cold traps fabricated from 0.75-in.-OD tubing and cooled by a dry ice-trichloroethylene mixture. Alternatively, the UF_6 was collected in a 10-ft-long, 3-in.-ID nickel condenser which was equipped with an axially-located 0.75-in.-dia finned tube for additional heat-transfer surface. Trichloroethylene, circulated through a refrigeration unit, was used as condenser coolant. The condenser was equipped with flexible lines and mounted on a remote-reading scale in order to monitor collection rate by weight change. Data collected during operation of the condenser indicated a collection efficiency of about 96% and an equilibrium UF_6 vapor pressure of about 1 mm Hg; therefore, a sodium fluoride adsorber was also provided to complete the removal of UF_6 from the gas stream. This adsorber, 4 in. in OD and 18 in. long, mounted on flexible lines, was also weighable. A Lapp diaphragm gas compressor was used to recycle process off-gas as a means of increasing fluorine economy.

Fluorine was obtained from cylinders containing 6 lb of fluorine at 400 psi. Residual HF in the fluorine was removed by a sodium fluoride trap. The fluorine was metered to the reactor from a 17.6-cu-ft storage tank. Pressure drop on the tank was recorded and used as a measure of fluorine addition; fluorine flow rate was controlled manually or automatically by a system of orifices and flow-control valves. Similar orifice-control valve systems were used to measure oxygen and nitrogen flow rates to the reactor. Fluorine concentration in the reactor off-gas was measured in two ways: (1) samples of gas were taken and reacted with mercury in a calibrated volume, and (2) continuous measurement of fluorine concentration in the gas stream was obtained by means of a thermal conductivity cell. This analytical equipment is described in greater detail below.

The uranium dioxide pellets used were nominally of reactor-grade material, sintered in hydrogen or inert gas, with densities of at least 93% of theoretical. It is believed that these pellets are typical of reactor fuel material.² The inert fluidizable solids consisted of fused magnesium fluoride, commercial-grade calcium fluoride, fused reagent-grade calcium fluoride, zirconium tetrafluoride, and refractory-grain, recrystallized α -alumina.

B. Special Equipment

In the initial design, and later in the actual development, of the fluorination step, special equipment was provided to meet the needs of the pilot plant. This equipment included the systems for supply of fluorine gas, analysis of fluorine gas, automatic temperature control of the reactor, and the charging of pellets to the reactor.

1. Fluorine Supply

Fluorine was supplied to the reactor system from a high-pressure manifold which contained 6-lb (400 psi) cylinders of fluorine.³ The manifold (see Fig. 3) was contained in a steel enclosure behind 18-in.-thick concrete walls. The manifold valves were operated by handles extended through the steel walls,

and the cylinder valves were opened remotely with handles extended through the concrete walls. Fluorine was passed from the cylinders through NaF traps for HF removal and then to a 17.6-cu ft storage tank for pressure reduction. The storage tank was maintained at pressures from 40 to 60 psig.

108-3504

Fig. 3. High-pressure Fluorine Manifold and Supply System

a metal flask with a stirrer to provide adequate contacting. This unit was permanently attached to the sample manifold and operated through valves, so that there was no need for uncoupling the flask for agitation or pressure measurement. In order to eliminate possible gas leakage at the stirrer-shaft seal, a magnetically driven stirrer was designed.

A schematic diagram of the analyzer assembly is shown in Fig. 4. The body of the fluorine analyzer was fabricated from a

2. Fluorine Analysis

a. Batch Samples

The reaction of liquid mercury with fluorine has long been used as a method of fluorine analysis. In the common application of this method, a volume of fluorine in a Pyrex flask is contacted with mercury by vigorously shaking the flask by hand; without shaking, a thin film of fluoride prevents reaction. With a sensitive means of pressure measurement, such as a manometer, this method has been successful for analysis of gases with compositions ranging from about 0.5 to 99.5% fluorine.⁴

In order to increase the speed and safety of this analysis, the method was modified by use of

Fig. 5. Schematic Diagram of Fluorine Analyzer System

The use of the gas-analysis system was a significant improvement over the manual methods of contacting fluorine with mercury. The analysis of a sample proceeded smoothly and no difficulties were encountered with the system in about 35 fluorination runs. With this method of gas analysis, fluorine concentration in a gas sample was routinely obtained in approximately 0.5 to 0.75 hr.

b. Continuous Analysis

The continuous analysis of gaseous mixtures by thermal conductivity methods is well-known. The method depends on the ability of gas molecules to transfer heat by diffusion and collision. This ability is different for every gas or gas mixture; hence, the method is nonspecific and ideally suited for binary gas mixtures. The method is also applicable to the analysis of a single gas in multicomponent mixtures provided that the concentrations of other species in the mixture remain relatively constant.

In the usual application of thermal conductivity cells to the analysis of a gas, four heated filaments are used as the legs of a Wheatstone bridge. The reference gas of known composition is passed over two filaments of the bridge (reference side of cell) and the gas of unknown composition is passed over the remaining elements (sample side). The cell filaments are normally constructed from metals with a high temperature coefficient of resistivity; hence, displacement from thermal equilibrium between the reference and sample sides of the cell will unbalance the bridge. The degree of unbalance measured by the potentiometer is a function of the thermal conductivity and the concentration of the component of interest in the sample gas.

The continuous fluorine analysis of fluorinator effluent gas was carried out with a Gow-Mac* Model 9454 thermal conductivity

*Gow-Mac Instrument Company, Madison, N. J.

cell and 405-1 Power Supply. The cell contained four nickel filaments in a $2 \times 2 \times 1\frac{1}{8}$ -in. metal block. The block was heated above ambient temperatures in an insulated, thermostated enclosure which insured uniform temperatures in the metal surrounding the filaments. The cell was a fast-response, diffusion-type cell which produced an output relatively independent of sample flow rate from 50 to 1000 cc/min.

The relation of the continuous gas-analysis system and the fluorination system is shown in Fig. 6. Since the reactor effluent contained several gases (O_2 , N_2 , and F_2) whose thermal conductivities differed by only 0.05% at the pressures and temperature of interest, it was not possible to use the thermal conductivity method directly. Hence, the principle of substitution⁵ of one gas for another was employed. The quantitative substitution of chlorine for fluorine between the reference and sample sides of the cell provided a component in the gas stream with a thermal conductivity $1/3$ that of oxygen and nitrogen; therefore, by suitable calibration of the cell, a continuous fluorine analysis of the process off-gas was available.

Fig. 6. Continuous Fluorine Analysis of Fluorinator Effluent Gas by Thermal Conductivity Methods

The cell was calibrated against known mixtures of chlorine in nitrogen and of fluorine in nitrogen. The replacement reaction in the NaCl trap was determined to be efficient up to 96% of the stoichiometric equivalent. The trap was maintained at ambient temperatures in order to prevent formation of chlorine-fluorine compounds.

The thermal conductivity cell was operational for Run 70 and was used for all subsequent runs in this development study. Spot checks against fluorine analysis by reaction with mercury indicated that agreement between the results of the two kinds of analysis was within 10%. In Run 76, a fluorine utilization (to UF_6) of 90% for the first 6 hr of operation was calculated from data obtained by means of the thermal conductivity cell; this result compared favorably with the fluorine utilization of 88% calculated from the total fluorine fed to the reactor and the total UF_6 collected in the condenser.

3. Automatic Temperature Control of the Reactor

Because of the highly exothermic nature of the fluorination reaction it was necessary to regulate the temperature of the system, thereby imposing a limitation on the reaction rate relative to the heat transfer achieved in the reaction zone. In the early phases of the experimental program fluorine feed was set at programmed rates, and automatic temperature control of the fluorination was provided by variation of the coolant air rate past the external fins of the reactor. Coolant rate was controlled by an automatic butterfly valve which regulated the air rate in proportion to the temperature level in the fluidized-packed bed. This system operated usefully under most conditions; however, temperature response of the reaction system under coolant regulation was slow. This fact became evident because the coolant flow rate was often kept near or at the maxi-

Fig. 7. Fluorine Flow Control System for Temperature Control in Uranium Dioxide Pellet Fluorinations

imum value of 400 cfm, thereby limiting reaction rates. Control by this method was limited by radial heat transfer, which varied in a complex manner under reaction conditions in the fluidized-packed bed.⁶ Therefore, the temperature-cooled system was modified so that (i) the fluorine feed rate was automatically regulated by reactor temperature and (ii) external cooling, when required, was provided by manual regulation of the coolant air flow. The final control system is shown in Fig. 7. Fluorine

from the 17.6-cu ft storage tank was throttled to provide a constant pressure in the smaller surge tank. According to reactor temperature and the programmed control temperature, a pneumatic valve positioner operated a control valve which regulated the flow of fluorine from the surge tank to the reactor. The valve positioner was regulated by a standard single-point potentiometer recorder-controller with proportional and reset functions.

Column temperatures obtained during a typical fluorination (Run 29) are shown in Fig. 8. The control temperature was measured through a horizontal thermowell at the center of a 6-in.-deep pellet bed (at the midpoint). Temperature was also measured at the same elevation but at a point 1 in. from the wall, through a vertical thermowell which entered from the bottom of the reactor. The wall temperature was measured through a horizontal thermowell flush with the inside wall of the column. External wall and fin temperatures were measured by thermocouple junctions welded in place.

108-4659

Fig. 8. Column Temperatures during Run 29

In Run 29 the 6-in. bed of pellets was reacted in a total of 6 hr at an average rate of $25 \text{ lb UF}_6/(\text{hr})(\text{sq ft})$; the maximum rate of $45 \text{ lb UF}_6/(\text{hr})(\text{sq ft})$ was reached at 240 min of operation (see Fig. 8). After 240 min of operation, the reactor was heated to maintain column temperatures. Under these conditions, the system of temperature control (temperature regulated by control of fluorine feed rate and manual regulation of coolant air) maintained the programmed control temperature of 530°C while the bed of pellets was reacted. The uniformity of the temperature at the center of the bed indicated the effectiveness of automatic fluorine regulation as a means of temperature control.

4. Pellet Charger

In these pilot-plant development studies, it was desirable, for several reasons, to demonstrate the charging of UO_2 pellets during fluorination. In principle, the successful charging of pellets on a pilot-plant scale would indicate the feasibility for continuous operation or, conversely, for batch operation with limited pellet-bed heights, yet with high throughput. In pilot-plant experiments, the pellet charger provided a means of stabilizing pellet-bed heights while the effects of other parameters were investigated.

The pellet-charging apparatus is shown in Fig. 9. The charger was constructed from a 1.5-in. Teflon-sleeved plug valve surmounted by a

Fig. 9. Uranium Dioxide Pellet Charger

length of 1.5-in.-dia pipe. In order to hold the pellets in position and to prevent bridging in the charger, two 0.5-in.-ID tubes were placed inside the pipe to accept the pellets. The tubes extended to within 0.25 in. of the valve plug to ensure that the pellets remained in the tubes as the valve was operated. Pellets were individually charged to each tube; a close fit between the pellet diameter and the internal diameter of the tubes was used to obtain an air-cushion effect to limit pellet acceleration in the tubes. The pellet-charging apparatus had sufficient capacity so that a 3-in. bed of pellets (4.8 lb) could be charged to the fluorinator in one operation. The pellet-charging apparatus was used on a routine basis during Runs 56 through 60.

C. Procedure

The pilot-plant facility was designed so that a number of operational methods for fluorinating UO_2 pellets could be investigated. The three general methods of operation are outlined in

Fig. 10; these included single-pass gas flow, two-zone oxidation-fluorination, and recycled gas flow.

Under each general method a number of options were available.

1. Single-pass gas flow:

- a. $\text{F}_2\text{-N}_2$ feed;
- b. $\text{F}_2\text{-O}_2$ feed;

- c. F_2 - N_2 - O_2 feed.
2. Two-zone oxidation-fluorination:
 - a. O_2 - N_2 feed to bottom, F_2 feed to top of pellet bed;
 - b. O_2 - N_2 feed to bottom, F_2 feed plus diluent to top of pellet bed.
3. Recycled gas flow:
 - a. Recycled effluent (O_2 , N_2 , F_2) plus F_2 makeup feed;
 - b. Recycled effluent (O_2 , N_2 , F_2) plus F_2 - N_2 makeup feed.

Fig. 10 Operational Methods for the Fluorination of Uranium Dioxide Pellets

In a typical operating procedure, a weighed quantity of fluid-bed material was placed in the reactor and fluidized with nitrogen. A weighed quantity of uranium dioxide pellets corresponding to a desired packed height (e.g., 19.4 lb for a 12-in. bed) was then added to the fluidized alumina and allowed to settle into place. Fluidization by nitrogen was continued until the operating temperature was reached, at which point fluorine introduction was begun at programmed flow rates. Uranium hexafluoride production was monitored at half-hour intervals by weight change of the condenser or coiled cold traps. Once-through gas flow was maintained until most of the pellet bed had been reached; at this point high rates of uranium hexafluoride production and high fluorine utilization could no longer be maintained. The run was then either temporarily interrupted for inspection of the bed or was continued by operating with fluorine recycle to remove the uranium compounds remaining in the alumina bed.

III. RESULTS AND DISCUSSION

A. Preliminary Fluorination Experiments

A series of preliminary experiments was carried out to determine the effects of process variables in the direct fluorination of UO_2 pellets.

These were carried out in a 3-in.-dia reactor which had been used for fluorination studies in the Aqueous Dry Fluorination Process.³ A schematic diagram of this equipment is shown in Fig. 11. The effects of fluorine concentration, pellet-bed height, and fines production on reaction rates were observed. The operating conditions for this series are given in Table 1.

Fig. 11

Fluid-bed Reactor for Preliminary Studies of the Fluorination of Uranium Dioxide Pellets

108-3818

TABLE 1. Summary of Operating Conditions for Preliminary Fluorination Runs

3-in.-dia fluidized-bed reactor
0.5-in.-dia by 0.5-in.-long UO_2 pellets
Magnesium fluoride fluid bed

Run	F_2 (%)	N_2 (%)	Temp (°C)	Pellet-bed Height (in.)	Gas Flow Rate (ft/sec)	Fluid-bed Static Height (in.)	Time (hr)
1	10	90 ^a	400	3	0.7	6	3
2	10	90	400	3	0.7	6	2.5
3	-	100	400	3	0.7	6	2.5
4	10	90	500	3	0.35	12	3
6	10	90	500	3	0.35	12	3
7	20	80	500	3	0.35	12	1.5
8	20	80	500	(fines) ^b	0.35	12	<0.2
9	30	70	500	3	0.35	12	1
10	5	95	500	(fines) ^b	0.35	12	<0.2
11	20	80	500	9	0.35	18	1.5
12	20	80	500	6	0.35	15	1.5
14	20	80	400	9	0.5	60	1.5

^aAir was used in this run.

^bFine particles of uranium compounds resulting from incomplete reaction of UO_2 pellets with fluorine.

1. Effect of Fluorine Concentration

The effect of fluorine concentration on the reaction rate and the fluorine utilization efficiency was studied in Runs 6, 7, and 9. These runs were carried out at a temperature of 500°C and a superficial gas velocity of 0.35 ft/sec, with a pellet bed 3 in. deep, and a 6-in.-deep bed* of 60 to 80 mesh MgF_2 . Inlet fluorine concentrations were varied in the range 10 to

Fig. 12. Uranium Hexafluoride Production and Fluorine Utilization as a Function of Inlet Fluorine Concentration

30%, and the duration of each run was adjusted so that approximately equal amounts of UF_6 were collected. For these runs, the fluorine utilization efficiencies were based on the amount of fluorine introduced and the UF_6 product collected.

The variations in UF_6 production rates and fluorine utilization with inlet fluorine concentration are shown in Fig. 12. As expected, the rate of UF_6 production was practically linearly dependent upon the inlet fluorine concentration. Although UF_6 production rates increased, fluorine utilization decreased when the inlet fluorine

concentration was raised from 20 to 30%, indicating that for the same linear gas velocity greater losses of fluorine could be anticipated at the higher fluorine concentrations. It should be noted, however, that the lowest fluorine utilization was 62% for the three inlet fluorine concentrations.

2. Effect of Pellet-bed Height

Runs 7, 11, and 12 were carried out to determine the effect of the height of the stacked bed of pellets. In these runs fluorine inlet concentration was maintained at 20%, and the height of the pellet bed was varied from 3 to 9 in. As before, approximately equal amounts of fluorine were used in each run. Total fluorine utilization was calculated from the fluorine input and from fluorine analysis of the reactor effluent gas; the difference between total fluorine utilization and fluorine consumed to form UF_6 represents the fluorine consumed in the formation of intermediate uranium fluorides. If no intermediate uranium fluorides are formed, fluorine consumed to form UF_6 and the total fluorine utilization would be identical.

With the shallow (3 in.) bed of pellets there was no evidence of the formation of intermediate uranium fluorides; accordingly, fluorine utilization based upon collection of UF_6 product was an accurate indication of the fluorine utilization for a run. With deeper beds of pellets, however,

*Static height in an empty column.

formation of intermediate uranium fluorides became significant (see, for example, Sect. III.A.3), and the total utilization of fluorine was that resulting both from formation of intermediate compounds and from UF_6 production.

Fig. 13. Uranium Hexafluoride Production and Fluorine Utilization as a Function of Pellet-bed Height

The variation of UF_6 rates and total utilization as a function of pellet bed height for equal amounts of fluorine fed to the reactor is shown in Fig. 13. The slight decrease in UF_6 rates and the concurrent increase in total fluorine utilization were attributed to the formation of intermediate uranium fluorides. As shown in Table 2, the decreased UF_6 production rates corresponded to a lower fluorine utilization to form UF_6 and to a higher fluorine utilization to form the intermediate uranium

fluorides. These effects accompanied an increase in total fluorine utilization which was due to the increase in surface area of reactive solids with an increase in bed height.

TABLE 2. Effect of Pellet-bed Height on Fluorine Utilization

		Temperature: 500°C		
		Fluorine Concentration: 20%		
Run	Pellet-bed Height (in.)	Fluorine Utilized to Form UF_6 (%)	Fluorine Utilized to Form Uranium Fluorides (%)	Total Fluorine Utilization (%)
7	3	77	0	77
12	6	62	26	88
11	9	55	41	96

3. Production of Intermediate Fines of Uranium Fluoride

The reactor used in the exploratory series of runs was not equipped to return fines from the process filter to the reactor. The fines which elutriated from the reactor disengaging section were thus retained on the process filter. In Runs 1 and 2, a substantial quantity of fines was collected by the filter when 3-in. beds of pellets were fluorinated with 10% F_2 in air or with 10% F_2 in nitrogen at 400°C. Fines collection on the filter was not significant in Runs 6, 7, and 9, in which 3-in. deep pellet beds were fluorinated at 500°C with 10 to 30% F_2 in nitrogen. In Runs 11 and 12, which

utilized 6- and 9-in.-deep pellet beds, fluorination with 20% F_2 in nitrogen at 500°C did result in a substantial quantity of fines on the filter. It was observed that when substantial fines were collected by the filter, a significant quantity of fines was also present in the fluid-bed material.

The screen analyses of material taken from the filter and from the fluid bed for Run 11 are given in Table 3. The particle-size distribution indicates that practically all the fines were less than 200 mesh and that one-third of the fines had a particle size smaller than 325 mesh. Analysis of the fine material by X-ray diffraction showed the presence of UO_2F_2 as the major phase and of U_3O_8 as the minor phase. In the fines taken from the filter, no MgF_2 , UO_2 , or UF_4 was detected. These results indicated that fines production during fluorination was brought about by chemical reaction rather than by attrition of the pellets or the fluidized bed. This conclusion was further substantiated by a previous test (Run 3) when a bed of UO_2 pellets did not disintegrate after a 2.5-hr exposure to nitrogen at 400°C. The presence of a major phase of UO_2F_2 in the fines gave evidence that the mechanism of the fluorination reaction proceeded initially by formation of the intermediate UO_2F_2 followed by fluorination to UF_6 . The presence of a minor phase of U_3O_8 was also indicative of the fact that oxygen (a product of the UF_6 formation) reacted with UO_2 at significant rates even in the presence of fluorine.

TABLE 3. Screen Analysis of Fines Produced during Fluorination of Uranium Dioxide Pellets--Run 11^a

Mesh Size	Filter Fines (%)	Fluid-bed Residue (%)
-60 +100	-	69.7 ^b
-100 +200	4.5	5.3
-200 +325	62.8 ^c	16.8 ^c
-325	32.7 ^c	8.2 ^c
	100.0	100.0

^aFor run conditions see Table 1.

^bMostly 60 to 80 mesh MgF_2 .

^cBy X-ray diffraction--major phase (UO_2F_2); minor phase (U_3O_8).

Fines were returned to the reactor, in Runs 8 and 10, and fluorinated at 500°C in an effort to determine fluorination rates for the fine particles. In both cases, the fines were completely fluorinated in less than 13 min, thereby making it impossible to calculate a reaction rate. The fines reacted at a much higher rate than the UO_2 pellets and therefore enter quite significantly into the reaction mechanisms. The higher reaction rates with fines are attributed to the much larger specific surface area of the fines compared to that of the UO_2 pellets.

4. Effect of Height of Fluidized Bed

The effect of a deeper fluidized bed was determined in Run 14, carried out with a 9-in.-deep pellet bed and with 20% F_2 in nitrogen at 400°C. The pellets were submerged in a magnesium fluoride bed (60 to 100 mesh) which was 60 in. deep under static conditions. Run 14 was similar to Run 11 which was carried out at 500°C with a magnesium fluoride bed height of 18 in. (static).

The total amount of intermediate uranium fluoride fines (major phase UO_2F_2) which formed during Run 14 was about 40% higher than the fines formed in Run 11. This was attributed to the lower rate of reaction of UO_2F_2 to form UF_6 at 400°C and was evidenced by the fact that UF_6 collection rates were one-third the rates at 500°C.

The quantity of fines which collected on the process filter during Run 14 was about one-half the amount which collected during Run 11. Since the total amount of fines in the reactor was 40% higher during Run 14, these results gave a clear indication that deeper beds of fluidized solids reduced elutriation of fines from the reaction zone.

5. Kinetics of the Reaction

The kinetic mechanism of the direct fluorination reaction is important to the design of full-scale process equipment. From the results of this exploratory series of runs, it was shown that the fluorination of UO_2 to UF_6 proceeded in two steps: partial fluorination of UO_2 to UO_2F_2 , followed by complete fluorination of UO_2F_2 to UF_6 . It was also shown (in Run 14) that the rate-controlling step was the fluorination of UO_2F_2 to UF_6 and that the reaction rates for this latter step were higher by a factor of about 3 at 500°C than at 400°C. The rate of the overall fluorination (UO_2 to UF_6) was also shown to be proportional to fluorine concentration, indicating that the reaction has a first-order dependence on fluorine partial pressure.

In addition, oxygen released as a product in the overall fluorination reacted with the UO_2 pellets at significant rates to form U_3O_8 fines. When deeper beds of UO_2 pellets were used, formation of uranium fines (UO_2F_2 , U_3O_8) increased with a consequent increase in the total available surface area of reactive solids. This effect increased with pellet-bed height; consequently, with the deeper beds of pellets high fluorine utilization was demonstrated.

When the 6- and 9-in.-deep beds of pellets were fluorinated, a substantial part of the residual pellets agglomerated and were attached to the wall as a solid deposit; these deposits were found in the upper parts of the pellet bed. It appeared that the agglomeration was due to reaction of UF_6 with UO_2 to form UO_2F_2 , UF_4 , and other intermediate uranium fluorides.

This effect put an apparent limit on the height of the packed bed of pellets, and also influenced reaction rates and fluorine efficiencies when the batch reactions were carried to completion.

Fluorine concentrations and the height of the UO_2 pellet beds were varied in Runs 6, 7, 8, 9, 11, and 12, in which fluorine utilization ranged from 66.8 to 93.5%. These data were used to calculate the height of a reactor unit, defined by Hurt⁷ through the equation

$$\ln \frac{y_1}{y_2} = \frac{KaS}{G} L = \frac{L}{H}, \quad (1)$$

where

G = mass flow, mol/hr;

y_1 = inlet fluorine concentration, mole fraction;

y_2 = outlet fluorine concentration, mole fraction;

K = rate coefficient, mol/(hr)(sq ft)(Δy);

a = pellet interfacial surface area per unit volume;

S = cross-sectional area of column, sq ft;

L = pellet-bed height, ft;

$H = G/KaS$, height of a transfer unit, ft.

The calculations based on these runs showed: (1) that H was equal to 0.24 ft, (2) that the fluorine utilization was independent of inlet concentration but dependent upon bed height, and (3) that H decreased with decreasing gas rates. However, it should be noted that requirements as to heat transfer and fluidization quality placed restrictive limits on the extent to which operating conditions could be varied.

6. Operational Experience

Although the fluorination of uranium dioxide is highly exothermic, no problems of temperature control were encountered with the operating conditions in this exploratory series of runs. This beneficial effect was due to the use of an inert fluidized bed which provided adequate heat transfer from the pellet bed to the reactor wall.

Temperature profiles taken during Runs 6, 7, and 9 showed variations of less than $\pm 25^\circ\text{C}$ throughout the reactor for an entire run. In Run 11, temperatures measured by a thermocouple inserted into a pellet which was located at the vertical midpoint of the pellet bed were compared with temperatures measured in a vertical thermowell at the center axis of the reactor. (The pellet thermocouple was located midway between the vertical thermowell and the reactor wall.) The pellet temperature was 50°C lower at

the start of the run and 20°C higher at the conclusion, indicating that the maximum temperature difference between the pellet and the thermowell was 50°C and that actual pellet temperatures were very close to the measured fluidized-packed-bed reaction temperature.

7. Effect of Operational Parameters on the Process for the Direct Fluorination of UO₂

The observed qualitative effects of the operational parameters which were studied during this exploratory series of runs are summarized in Table 4, together with other significant process effects.

TABLE 4. Effect of Operation Parameters on the Process for the Direct Fluorination of UO₂ Pellets

Decreased Temperature	← Temperature →	Increased Temperature
Decreased Reactor Corrosion Less Danger of Caking Decreased Reaction Rate		Increased UF ₆ Production Decreased Fines Accumulation Increased Reactor Corrosion
Decreased Concentration	← Fluorine →	Increased Concentration
Better Temperature Control Lower Reaction Rates Possible Intermediate Formation		Decreased Fines Production Increased UF ₆ Production
Decreased Height	← UO ₂ Bed Height →	Increased Height
Decreased UO ₂ Pellet Caking		Increased Fluorine Utilization
Decreased Height	← Fluidized Bed Height →	Increased Height
Decreased Fines Retention Decreased Area for Heat Transfer		Increased Area for Heat Transfer Increased Dilution of Fission Products Decreased Fines Elutriation
Decreased Size	← Fluidized Particle Size →	Increased Size
Better Solids Motion in Voids of Pellet Bed Better Fines Retention Lower Minimum Fluidization Velocities		Less Chance of Sintering Higher Allowable Gas Velocities
Decreased Velocity	← Gas Velocity →	Increased Velocity
Increased Fluorine Utilization Efficiency Decreased Fines Elutriation		Better Heat Transfer Less Tendency for Caking

B. Effect of Conditions of Pellet Manufacture on the Fluorination Reaction

The prior history and property of UO₂ pellets used in this study are given in Table 5. The conditions of their manufacture appeared to affect the rates of reaction with fluorine. Pellets sintered in an inert atmosphere disintegrated into fines when exposed to fluorine, whereas pellets sintered in a hydrogen atmosphere remained comparatively intact. Higher rates of reaction were obtained with the fine particles because of their large reactive surface area. Also, reaction of the fines favored temperature control because the heat of reaction was distributed throughout the fluidized bed. Thus, processing of the hydrogen-fired pellets was relatively more difficult because of less fines production and less favorable heat transport from the fluidized-packed bed.

TABLE 5. Prior History and Properties of Pellets Used in Fluorination Runs

Type	Inert fired	Hydrogen fired
Manufacturer	Davidson Chemical Co.	Nuclear Materials and Equipment Co.
Purity	Reactor grade	Reactor grade
Source	Ammonium diuranate calcined at 770°C	Ammonium diuranate plus recycled U_3O_8
Sintering	Fired in inert atmosphere at 1720°C	Fired in dry hydrogen at 1700°C for 4 hr
Density, g/cc	10.49	10.26
% Theoretical density ^a	95.6	93.6

^aBased on a theoretical density of 10.97 g/cc.⁸

The reactivities of the hydrogen-fired and the inert-fired pellets are compared in Table 6. At 400°C, the tendency for both types of pellets to form intermediate uranium fluoride fines is evident by the amount of the original UO_2 charge which was converted to UO_2F_2 . This tendency indicates that the rate of UF_6 formation is affected by the relatively strong temperature dependence in the fluorination of UO_2F_2 . The greater reactivity of the inert-fired pellets at both 400°C and 500°C is shown by the higher fluorine utilization efficiencies reported in Table 6.

TABLE 6. Effect of Prior History on the Fluorination of UO_2 Pellets

Equipment:		3-in.-dia fluid-bed reactor						
Pressure:		1 atm						
Gas Rate:		0.5 cu ft/min (25°C)						
Fluid Bed:		60-200 mesh MgF_2						
Fluorine Concentration:		20%						
Diluent:		Nitrogen						

Run	Pellet Firing Atmosphere	Pellet-bed Height (in.)	Run Time (hr)	Temp (°C)	Stoichiometric ^a Equivalents Fluorine Fed	UO ₂ Conversion		Total ^b Fluorine Utilization (%)
						UO ₂ F ₂ (%)	UF ₆ (%)	
14	Inert	9	1.5	400	0.18	21.5	3.0	79
22	H ₂	3	4.0	400	1.30	33.6	27.0	31
7	Inert	3	1.5	500	0.53	6.6	32.0	82
24	H ₂	3	3.5	500	1.38	3.8	27.0	21 ^c

^aOne-third x moles fluorine fed/moles UO_2 charged (based on the reaction $UO_2 + 3F_2 \rightarrow UF_6 + O_2$).

^bFluorine consumed to form UO_2F_2 and UF_6 .

^cFor the last 0.5 hr of this run, fluorine concentration was increased to 40% and the utilization increased to 29%.

On the basis of specifications for reactor-grade fuel, it was believed that the hydrogen-fired pellet would be more representative of reactor fuel material than the inert-fired pellets. Consequently, in Run 29, and all subsequent runs the hydrogen-fired pellets were utilized.

C. Effect of Fluid-bed Material

The use of a fluidized bed of inert solids offers several advantages in the reprocessing of spent fuel by fluoride volatility techniques. The fluid bed aids in heat removal from the exothermic reactions involved, dilutes the solid reagents, distributes the gaseous reagents, retains solid reagent fines during reaction, and, ultimately, dilutes and transports the radioactive residues. On the other hand, the retention of uranium and plutonium on the surface of the inert solids makes product recovery more difficult.

A satisfactory fluidizable medium for a fluid-bed fluoride volatility process must possess certain characteristics which include: (1) chemical inertness, (2) high melting point, and (3) mechanical stability. In addition, since the fluidized solids will be discarded as radioactive waste from the process, a low retention of uranium and plutonium on the bed material is also required. The retention of uranium and plutonium was determined in separate laboratory studies,⁹ which showed that virtually complete uranium removal was possible and that a final choice of the inert solids was dependent only upon plutonium removal.

The fluidizable solids used in this pilot-plant development work included (1) fused magnesium fluoride (a byproduct from a uranium reduction process), (2) commercial-grade calcium fluoride (fluorspar), (3) fused reagent-grade calcium fluoride, (4) zirconium tetrafluoride, and (5) refractory-grain, recrystallized α -alumina.

With the exception of fluorspar, these materials were inert to the chemical action of fluorine. Fluorspar was found to be satisfactorily inert for use during hydrofluorination of Zircaloy in decladding tests; however, when exposed to fluorine, the fluorspar caked. In a separate test, it was also found that the fluorspar was softened and reduced in size after a 2-hr exposure to 50% F_2 in nitrogen at 500°C. It was concluded from these results that fluorine attacked the impurities in the fluorspar and structurally weakened the calcium fluoride granules. This conclusion was verified by the fact that fused, reagent-grade calcium fluoride was stable during both hydrofluorination and fluorination (as in Run 21).

Zirconium tetrafluoride was tested in a single experiment (Run 27) because of the possibility that this material might be generated as a byproduct in the decladding step by hydrofluorination of Zircaloy cladding. By screen analysis and visual observation, the zirconium tetrafluoride was found to be mechanically and chemically stable when used at 500°C with 20 to 40% fluorine during fluorination of an 800-g batch of UO_2 pellets.

A bed of magnesium fluoride was reused in 24 of the first 29 runs. After this extensive exposure to fluorine at elevated temperatures, the material showed no signs of decrepitation or deterioration. The main disadvantage in the use of this material stems from the fact that it is a byproduct slag from uranium metal reduction and is not commercially available.

Fused, refractory-grain α -alumina was used in Run 36 and in all subsequent runs which utilized fluidized beds. This material is commercially available from several sources. In these studies, Type 38 and high-purity Blue Label Alundum, products of the Norton Company, Worcester, Mass., were used. These materials exhibited the properties of chemical inertness, high melting point, and mechanical stability. The particle-size distributions for the Type 38 and Blue Label Alundum mixtures are given in Fig. 14. The major impurities¹⁰ are listed in Table 7.

Symbol	Alundum Grade	Composition (w/o)	Nominal Particle Size (U S Mesh)	Maximum Size Range (U S Mesh)	Used in Runs
○	Type 38	100	54-100	-40 +170	Prior to Run 65
□	Blue Label	50	60	-40 +120	Run 65
◇	Blue Label	50	90		
		32	60	-40 +170	Runs 66 to 76
		56	90		
		22	120		

108-6528 Rev.

Fig. 14. Particle-size Distribution of Norton Alundum Mixtures Used in Uranium Dioxide Pellet Fluorination Runs

TABLE 7. Spectrographic Analysis of Norton's Alundum

Element	Blue Label (%)	Type 38 (%)	Element	Blue Label (%)	Type 38 (%)
Fe	0.01	0.03	Si	<0.01	0.08
Mg	<0.01	<0.01	Ti	<0.01	<0.01
Na	<0.01	0.2	Zr	0.01	<0.01

In Runs 65 to 76, high-purity Blue Label Alundum was used in preference to Type 38, calcium fluoride, and zirconium tetrafluoride because it was determined that this material retained the least amount of plutonium after fluorination of $\text{UO}_2\text{-PuO}_2$ in laboratory experiments.⁹ No further consideration was given to magnesium fluoride because of limited commercial supplies of this material.

D. Effect of Fluid-bed Height

The static height of the fluidized beds was varied from 6 to 60 in. In general, the height of the fluidized bed exceeded that of the pellet bed. Temperature control apparently did not depend on the height of the fluidized bed. The main effect of increased height of fluidized beds was to improve fines retention by decreasing the elutriation of fines from the bed which, in turn, tended to increase the fluorine efficiency (see Table 4, p. 28).

E. Fluorination of Uranium Dioxide Pellets

1. Gas-solid Reactions, Direct Fluorination

Under practical reaction conditions in a fluidized-packed bed, the direct fluorination of uranium dioxide pellets has been found to proceed in two steps:

In the first step fluorine reacts with the pellet surface to produce UO_2F_2 , which tends to spall as a finely divided solid. In the case of ideal fluidization of inert material in the voids of the pellet bed, these fines are distributed throughout the fluid bed; when fluidization is not ideal, the fines tend to accumulate in the voids. In the second step, the UO_2F_2 powder reacts to form volatile UF_6 . The formation and removal of UO_2F_2 occurs simultaneously during the fluorination of a batch of pellets.

At the beginning of a batch fluorination, fluorine is consumed to form UO_2F_2 and little or no UF_6 is produced. The amount of UO_2F_2 fines increases until it competes successfully for fluorine and the rate of removal of UO_2F_2 fines by fluorination balances the rate of production of the fines. The pellets gradually diminish in size during the fluorination. This behavior is typical of batch fluorinations which exhibited an initial induction period (when virtually no UF_6 was collected) and a major reaction period (when fluorination rates and high fluorine utilization was obtained). The period of high reaction rate was followed by a period in which the rate of UF_6 production abruptly declined as the pellet material was depleted. Typically, the major part of the run showed a fairly constant rate of UF_6 production.

Oxygen also reacts with the UO_2 pellets:

The U_3O_8 tends to spall from the pellet surface as fine material of high surface area, similarly to the behavior of UO_2F_2 described above. This reaction proceeds whether oxygen is alone or in the presence of fluorine. The overall effect of the oxygen in fluorination of the pellets is to increase the rate and efficiency of fluorination (this effect is shown in Runs 31 to 34, Table 9, p. 36). In these experiments, higher production rates of UF_6 were correlated with higher concentrations of uranium-bearing fines in the inert fluid bed.

Oxygen is normally present as a byproduct of the fluorination. If desired, oxygen may also be introduced to the pellet bed as a fluorine diluent or by recycle of the process effluent gas since no oxygen is retained by the UF_6 product.

2. Steady-state Effects of Gas Velocity on Fluorination Rates

The effect of gas velocity, under steady-state conditions, was investigated with superficial gas velocities in the range from 0.5 to 1.35 ft/sec at 500°C with 10% F_2 in nitrogen gas mixtures. Steady-state conditions were achieved by maintaining the height of the pellet bed at a constant level of 6 in. At one-hour intervals whole pellets were charged to the reactor, the weight added being determined from the total UF_6 collection during the interval. The variation of UF_6 production rate with gas velocity is given in Table 8.

TABLE 8. Effect of Gas Velocity upon Uranium Hexafluoride Production under Approximately Steady-state Conditions

UO_2 Pellets:		0.5-in. dia x 0.5 in. long		
Weight of Pellets:		9.7 lb (pellets added during run)		
Fluidized-packed Bed:		6 in.		
Alumina Charge:		5.8 lb		
Alumina Bed Height: ^a		12 in.		
Weight Ratio $\text{Al}_2\text{O}_3/\text{UO}_2$:		0.6		
Fluorine Concentration:		10%, diluent N_2		
Temperature:		500°C		
Run	Duration (hr)	Fluidization Velocity ^b (ft/sec)	Fluorine Utilization ^c (%)	UF_6 Production Rate [lb/(hr)(sq ft)]
56	4	0.5	24.5	5.3
57	4.5	1.0	17.4	6.4
58	4	1.35	17.5	7.7

^aBased on empty column under static conditions.

^bBased on cross-sectional area of column at 500°C and 1 atm.

^cBased on rate of production of uranium hexafluoride.

The rate of UF_6 production increased about 40% for an increase in gas rate of 170%. Under the processing conditions for these experiments, the data imply that the rate of fluorination increased as a function of gas rate to the $1/3$ power. Because of the small effect of the gas rate, fluorine utilization was correspondingly lower at the higher gas rates. Thus, it was demonstrated that relatively low fluorine utilization could be expected when fluorinating a 6-in. batch of pellets with no recycle of process effluent gas and no oxygen present in the feed gas.

3. Fluorination of UO_2 Pellets without a Fluid Bed

The primary function of the fluidized bed of inert solids in the fluoride volatility process is to provide rapid transfer of the heat produced by the exothermic reactions. Since the inert material may retain some uranium and plutonium after fluorination, the fluidized bed introduces a source of potential loss of fissionable material. In addition, the fluid bed restricts gas velocities to the range suitable for fluidization. Also, the fluid-bed material may be susceptible to caking. For these reasons, fluorination of UO_2 pellets without the use of a fluid bed was given some consideration as an alternative processing technique.

In the initial test of this technique (Run 30), a 6-in. bed of 0.5-in.-dia x 0.5-in., cylindrical pellets was fluorinated for 9.5 hr at $505 \pm 10^\circ\text{C}$. Fluorine concentration in nitrogen was varied from 20 to 52%. The average rate of UF_6 collection during the run was $19.4 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$. Ninety five percent of the pellet charge was reacted to UF_6 , and the fluorine utilization was 57%. No problems with fines were encountered and none were found in the pellet residue. In these respects, this run did not differ appreciably from previous runs with fluid beds.

However, the run did differ in that the wall temperature was maintained at 50°C by maximum flow (400 cfm) of cooling air past the fins. Under the assumed conditions of a 6-in. effective pellet-bed height and a heat-transfer film coefficient of $25 \text{ Btu}/(\text{hr})(\text{sq ft})(^\circ\text{F})$ at the reactor wall, the calculated effective thermal conductivity of the pellet bed was $0.5 \text{ Btu}/(\text{hr})(\text{sq ft})(^\circ\text{F}/\text{ft})$. This value was equal to that calculated for a previous run (Run 29) in which poor fluidization was obtained. Under conditions of good fluidization quality, a thermal conductivity of $5 \text{ Btu}/(\text{hr})(\text{sq ft})(^\circ\text{F}/\text{ft})$ was normally achieved in the fluidized-packed bed.

In a second fluorination of a 6-in. bed of pellets (Run 35) the fluorination was completed in 10 hr with an overall fluorine utilization of 74% and an average production rate of $25 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$. The major difference between this run and Run 30 was that the process effluent gas was recycled to the reactor for the entire run. The recycle of gas contributed to the higher utilization of fluorine and also returned oxygen to the reactor, thereby causing the formation of U_3O_8 fines during the run. The presence of

U_3O_8 fines also contributed to the higher utilization of fluorine. No operational difficulties were experienced with the fines during the course of the run. However, as in Run 30, poor heat transfer between the pellet bed and the reactor wall was evident, with an overall temperature gradient of about 800°C while reactor wall temperatures were maintained at 65°C by the cooling air.

The two fluorinations of pellets without a fluid bed demonstrated that such an approach was feasible. The high-temperature differentials which were indicative of poor heat transfer may be considered an advantage insofar as reactor corrosion is concerned, because the extremely low wall temperatures would reduce corrosion of the reactor to negligible rates. However, control over reaction temperature would be severely limited by poor heat-transfer conditions. Reaction temperatures could be controlled by limiting the fluorine feed rates; however, this type of control system would also limit UF_6 production rates to undesirably low levels.

Since, in addition to improving heat transfer during fluorination, the fluidized bed material also aids in fission product removal from the reactor, the main interest of the fluorination program was concerned with pellet fluorinations carried out with a fluidized bed.

4. Effect of Oxygen on Batch Fluorination of UO_2 Pellets

The technical simplicity of recycling process effluent gas provides an economically feasible method for increasing the fluorine utilization in the batch fluorination of UO_2 pellets. The recycled effluent also contains oxygen. Oxidation of the pellets results in the release of U_3O_8 fines which contribute to higher fluorination rates and to higher fluorine utilization. Application of these desirable effects is tempered somewhat by the increased difficulty of process control with recycled effluent. Under full gas recycle, a high rate of UF_6 production increases the oxygen concentration in the system and, for a given fluorine input, decreases the fluorine concentration. Thus, conditions which lead to excessive buildup of fines in the reactor can occur; i.e., increased oxidation of UO_2 to U_3O_8 occurs because of increased oxygen levels, and formation of UO_2F_2 fines rather than UF_6 occurs simultaneously because of decreased fluorine levels. A buildup of a large quantity of fines in the reactor may result in poor fluidization of the bed with concomitant development of local hot spots and inadequate temperature control of the reaction. For both single-pass and recycled gas flows, the influence of oxygen on the fluorination rates and fluorine utilization is compared with that of nitrogen in Table 9. For the runs shown, processing conditions were similar except for the type of gas used to dilute the fluorine and for the total gas rates.

TABLE 9. Effect of Oxygen on the Fluorination of UO₂ Pellets

<u>UO₂ Pellets</u>	0.5-in. dia x 0.5 in. right circular cylinders
<u>Weight:</u>	9.9 lb
<u>Bed Height:</u>	6 in.
<u>Fluidized Bed</u>	
<u>Material:</u>	CaF ₂
<u>Size Limits:</u>	-40 +140 mesh
<u>Static Height:</u>	36 in.
<u>Temperature</u>	500°C

Run	<u>Fluorine Diluent</u>		Average Inlet F ₂ Conc. (%)	Average Superficial Velocity (ft/sec) ^b	<u>Extent of Reaction</u>		Fluorine Utilization to UF ₆ (%)	UF ₆ Production Rate [lb/(hr)(sq ft)]	Fluidization Heat Transfer ^c
	Gas	Rate (cfm) ^a			(%)	Time (hr)			
31	O ₂	0.2	45	0.32	96	11.5	45	27	poor
32	N ₂	0.4	42	0.62	80	12.0	16	18	good
33	Recycle ^d	0.6	40	0.66	80	4.8	71	35	poor
					95	7.0			
34	Recycled	0.6	42	0.56	80	4.6	62	41	good
					95	6.0			

^aAt 25°C and 1 atm.^bBased on reactor cross-sectional area at process conditions.^cGood heat transfer when temperature differential between the fluidized-packed bed and the reactor wall was 50°C; poor when differential was 400°C.^dOxygen supplied by recycle of process effluent gas.

Oxygen rather than nitrogen dilution of fluorine resulted in higher overall fluorination rates by a factor of 2 or 3. A significant increase in fluorine utilization was achieved when oxygen rather than nitrogen was used with single-pass gas flow, and a further increase was achieved when fluorine dilution was provided by recycled gas. The increased fluorination rates and fluorine utilization were attributed to formation of U₃O₈ fines. No operational difficulties were encountered with these fines although some differences between runs were noted for the fluidization heat-transfer characteristics. Specifically, these differences were attributed to low superficial gas velocity in Run 31 and to initial temperature surges caused by sudden introduction of oxygen in Run 33. Even though fluidization was poor in Run 33, maximum cycles in the control temperature of $\pm 30^\circ\text{C}$ were recorded; these fluctuations contrasted with $\pm 5^\circ\text{C}$ cycles when fluidization quality was good, namely, in Runs 32 and 34. In particular, Run 34 demonstrated that good-quality fluidization could be maintained at high fluorination rates and fluorine utilization even though oxygen was present in the recycled gas.

In several of these runs, the buildup of uranium fines (U₃O₈ and UO₂F₂) was followed by uranium analysis of fluid-bed samples. The variation of uranium concentration in the fluid bed is shown as a function of run time for Runs 31, 32, and 34 in Fig. 15. The concentration of uranium fines in the fluid bed is clearly much higher when oxygen rather than nitrogen dilution of fluorine was utilized. In the run with nitrogen dilution, Run 32, the level of uranium concentration in the fluid bed remained below 0.07 w/o for the entire run. This was significantly lower than the runs which utilized oxygen dilution, and this difference in fines formation accounts for the lower rate of fluorination and fluorine utilization reported in Table 9.

108-4663 Rev.

Fig. 15. Fines Concentration in Fluidized Bed, Runs 31, 32, and 34

observed by a comparison of Figs. 15 and 17. After 3 hr of operation (see Fig. 15) the fines concentration also decreased, significantly, from about 6 to 0.4 w/o. Thus, the decrease in fluorine utilization corresponded to a decrease in fines concentration in the bed.

108-4668 Rev.

Fig. 16. Fluorine Inlet Concentration and Fluorine Utilization for Run 32

The important effects of fines formation on the fluorination reaction is further demonstrated in Figs. 16 and 17, where fluorine inlet concentration and the fluorine utilization are shown as functions of run time for Runs 32 and 34. The fluorine utilization was based on fluorine analysis of reactor inlet and outlet gas samples. The analysis was carried out by reaction of the fluorine with mercury.

For the first 3 hr in Run 34, the fluorine utilization was high (nearly 100%); after 3.5 hr of operation, the utilization dropped quickly to less than 50% (see Fig. 17). The dependence of fluorine utilization on the fines present in the bed can be

108-4670 Rev.

Fig. 17. Fluorine Inlet Concentration and Fluorine Utilization for Run 34

In contrast to these results, the fluorine utilization in Run 32 (see Fig. 16) was less than 30% for most of the run. Since nitrogen does not react with the pellets, the fines concentration in the bed remained below 0.07 w/o for the entire run; consequently, fluorine utilization remained at low levels.

These results show that generally increased rates of fluorination and increased fluorine utilization are obtained when fluorine is diluted with oxygen rather than nitrogen. The higher rates and fluorine utilization have been related to the presence of reactive fines in the fluidized bed. Although the use of oxygen dilution increased the fluorine utilization, a further increase in fluorine utilization from about 45 to 67% was realized (see Table 9) when the process effluent gas was recycled.

5. Effect of Temperature on Fluorination Rates with Oxygen and Nitrogen Dilution of Fluorine

The effect of temperature on the rate of UO_2 pellet fluorination was investigated in the range from 350 to 500°C with both oxygen and nitrogen dilution of fluorine. In this series of experiments, Runs 36-39, it was intended to dilute the fluorine with nitrogen during the first 1.5 hr of operation and then with oxygen for an additional 1.5 hr. Fluorine concentration was maintained at a constant level for each run; however, the higher reaction rates with oxygen dilution at 450 and 500°C required that the fluorine-oxygen mixture be diluted further with nitrogen to reduce the rates and to maintain uniform temperatures.

The rates of UF_6 production as a function of temperature and diluent gas are presented in Table 10. Besides temperature, the rate of UF_6 production may depend on the particular pellet charge, the gas flow rates and composition, and possibly other special circumstances. However, the process conditions used to obtain these data are believed to be sufficiently similar so that the effect of temperature and fluorine diluent is indicated for typical operation.

TABLE 10 Uranium Hexafluoride Production Rates as a Function of Temperature and Fluorine Diluent

UO_2 Pellets: 0.5-in. dia x 0.5 in. right circular cylinders
 Alumina Bed Height: ~35 in.
 Alumina Particle Size: -40 +200 mesh
 Gas Rate: 0.5 cu ft/min at 25°C
 Pressure: 1 atm

Run	Temp (°C)	<u>Reactant Gas Mixture</u>			Run Time (hr)	<u>Average Rate of UF_6 Production (g/hr)</u>	
		N_2 (%)	O_2 (%)	F_2 (%)		N_2 Diluent	O_2 Diluent
36	350	77	-	23	1.5	7	-
		-	79	21	3.0	-	107
37	400	75	-	25	1.5	49	-
		-	78	22	3.0	-	278
38	450	80	-	20	1.5	116	-
		38	46	16	3.0	-	428
39	500	75	-	25	1.5	232	-
		38	46	16	3.0	-	710

The rate data were normalized with respect to fluorine concentration for calculation of a first-order reaction rate constant. The normalized data are shown in Fig. 18.

The value of the temperature coefficient (E') in the Arrhenius equation

$$k = Ae^{-E'/RT} \quad (5)$$

was 14 kcal/mol for fluorination with both oxygen and nitrogen diluent. This result was in agreement with earlier laboratory experiments.¹²

108-4669

Fig. 18. Fluid-bed Fluorination of Uranium Dioxide Pellets: Temperature Dependence

Figure 18 indicates that the rate of UF_6 formation increased as a function of temperature and that the rate is approximately three times faster at temperatures above 400°C with oxygen dilution of fluorine. The increased rate is caused by formation of U_3O_8 fine particles with a consequent increase in reactive solid surface area.

6. Effect of Oxygen on the Fluorination at Steady-state Conditions

The effect of oxygen upon the fluorination reaction was further studied in runs maintaining steady-state conditions with a constant fluidized-bed height of 6 in. Pellets were added to the reactor to maintain a 6-in. depth of pellets in the reactor; the method of pellet addition has been described (see Sect. II.B.4).

It was planned to study the effect of oxygen at 5, 15, and 30% of the total gas flow with a constant concentration of 20% fluorine. However, when the oxygen reached a concentration of 13% in the feed gas, the actual fluorine concentration was limited to only 15% by the automatic temperature regulation of fluorine feed, that is, with the oxygen level at 13%, the rate of formation of U_3O_8 fines was sufficient to decrease the quality of fluidization and heat transfer. These effects produced local hot spots such that the preset temperature control operated to limit the rate of fluorine addition to the column. It therefore appeared that with 20% fluorine in the feed gas and a constant pellet bed height of 6 in., the range of oxygen concentration from 5 to 13% was sufficient for rapid production of U_3O_8 fines. The results of these experiments, Runs 59 and 60, are summarized in Table 11.

TABLE 11. Effect of Oxygen on Uranium Hexafluoride Production Rates under Steady-state Conditions

Weight of Pellets:	9.7 lb (pellets added during run)
Fluidized-packed-bed Height:	6 in.
Alumina Charge:	11.7 lb
Alumina Bed Height: ^a	24 in.
Weight Ratio $\text{Al}_2\text{O}_3/\text{UO}_2$:	1.2
Temperature:	500°C

Run	Process Time (hr)	Fluidization Velocity ^b (ft/sec)	Fluidizing Gas				Fluorine Utilization ^c (%)	UF ₆ Production Rate [lb/(hr)(sq ft)]
			F ₂ (%)	O ₂ (%)	N ₂ (%)	(F ₂ /O ₂)		
59	5	1.0	20	5	75	4.0	53.5	37.2
60 ^d	2	1.1	15	13	72	1.1	75.6	40.2

^aStatic height in empty column.

^bBased on cross-sectional area of column at 500°C and 1 atm.

^cBased on rate of production of uranium hexafluoride.

^dApproximate steady-state conditions were achieved.

Although the UF₆ production rates [approximately 40 lb UF₆/(hr)(sq ft)] were nearly the same at both levels of oxygen input, the fluorine utilization (76%) with 13% oxygen was significantly higher than the 54% utilization obtained with 5% oxygen. This difference was attributed to the higher rates of U₃O₈ formation at the higher oxygen concentration.

On the basis of UF₆ collection rates and fluorine utilization, both levels of oxygen would be promising for a practical process; however, only the 5% oxygen level would be acceptable on the basis of fluidization quality. The data also suggest that a F₂/O₂ ratio in the feed gas which approaches unity would be unsatisfactory in that the rate of U₃O₈ production would exceed the rate of fines removal by fluorination to UF₆, thereby affecting fluidization quality and reducing heat transfer in the fluid bed.

F. Oxidation of Uranium Dioxide Pellets

Because of the demonstrated effects of oxygen upon the fluorination of UO₂ pellets, several pellet oxidations were carried out. In these experiments, the rate of oxidation was followed by Orsat analysis of reactor effluent gases; in two experiments, the Orsat analysis was supplemented by PVT measurements in a closed recycle system. Oxidation conditions and results for these runs are shown in Table 12. The oxidation rates given in the tables are regarded as approximate, and dependent on the equipment geometry and on the particular procedure used.

TABLE 12. Oxidation of Uranium Dioxide Pellets

3-in. packed bed of UO_2 pellets (2.2 kg).
 Approximate surface area
 of initial pellet bed: 1050 sq cm.
 Oxygen diluent: N_2 .

Run	Reactant Gas (% O_2)	Gas Flow Rate (cfm) ^d	Alumina Fluid-bed Weight (kg)	Gas-flow Scheme	Temp (°C)	Duration (hr)	Exit Gas (% O_2)	Averaged Approximate Reaction Rate ^a mg O_2 (min)(sq cm)
43	21	0.5	7.0	Single pass	300	0.5	20	0.1
					400	0.5	20	0.1
					500	0.5	17	0.5
					600	0.5	17	0.5
45	21	0.5	None	Single pass	500	6.0	- ^b	(0.1) ^b
48	32	0.6	7.0	Closed-loop recycle ^c	500	4.0	18	0.5
47	32	0.6	7.0	Closed-loop recycle ^c	600	1.3	22	1.5

^aRates shown are based on initial surface area of pellets.

^bOrsat gas analyses gave scattered results for this run.

^cClosed-loop recycle system is described in text and Fig. 19.

^dAt 25°C and 1 atm.

The rate of oxidation in Run 43 did not exhibit the expected trend with temperature, probably because the various temperature levels were applied successively to the same batch of pellets. However, the rate increase which occurred between 400 and 500°C is supported by differential thermal analyses

and thermogravimetric analyses reported in the literature.¹³ The average rates of oxidation without a fluid bed were shown to be less than rates obtained with a fluid bed at 500°C (see Run 45).

Fig. 19. Schematic Diagram of Closed-loop System for Batch Oxidation of Uranium Dioxide Pellets

In Runs 47 and 48, the equipment was modified to provide a close-loop system as shown in Fig. 19. With this modification it was possible to follow the oxidation by Orsat analysis and also by PVT measurements. Results obtained in this manner showed that the rate of oxidation at 600°C was approximately three times faster than the rate at 500°C. The oxidation rates at both temperatures were sufficiently

high to provide adequate U_3O_8 fines for practical production rates of UF_6 ; e.g., fluorination of all U_3O_8 fines formed at rates of $0.5 \text{ mg } O_2/(\text{min})(\text{sq cm})$ of initial pellet surface area) corresponds to production rates for UF_6 of $47 \text{ lb}/(\text{hr})(\text{sq ft})$, whereas the oxidation rate at 600°C corresponds to production of $140 \text{ lb } UF_6/(\text{hr})(\text{sq ft})$.

In Runs 47 and 48, oxidation of the 3-in. bed of pellets was complete in 4 hr at 500°C and in 1.3 hr at 600°C . Density measurements and X-ray diffraction analysis on the pellet residues showed that the product of the reaction was U_3O_8 . The U_3O_8 was present in the form of a fine powder. In

Run 45, a screen analysis of the U_3O_8 powder indicated that 79.3% of the powder was of less than $44\text{-}\mu$ diameter (-325 mesh). Since a portion of the powder agglomerated during the analysis a more accurate size distribution was obtained by a Coulter Counter Analysis. This analysis, shown in Fig. 20, indicated that the average particle of U_3O_8 was of about $12\text{-}\mu$ dia.

Fig. 20. Particle-size Distribution of U_3O_8 Fines, Run 45

1. Fluorination of Oxidized Pellets

As one alternative in the processing cycle, it was considered that complete oxidation of a pellet charge

followed by in situ fluorination of the U_3O_8 would result in improved UF_6 production rates and controlled temperatures in the reactor. Consequently, the U_3O_8 reaction products from two oxidation experiments, Runs 43 and 45, were fluorinated in place at 500°C with nitrogen-fluorine mixtures. In one case, Run 44, the U_3O_8 was fluorinated in the presence of a fluidized bed; in Run 46, the U_3O_8 was fluorinated without a fluidized bed.

In both fluorination experiments, high temperature differentials were encountered across the reaction zones. The temperature differentials gave an indication of poor heat transfer which resulted in rapid temperature increases with the addition of small amounts of fluorine.

The maximum rate of UF_6 collection in Run 44, $37.8 \text{ lb } UF_6/(\text{hr})(\text{sq ft})$, was substantially higher than the overall average rates of collection, 13.5 and 11 $\text{lb } UF_6/(\text{hr})(\text{sq ft})$, for Runs 44 and 46, respectively. Evidently, the combination of a large quantity of very reactive powders and

the poor quality of fluidization, owing to more than 15 w/o powder in the fluid bed, contributed to the high bed temperatures when fluorine was introduced to the reactor.

Although the rate of fluorination was not extremely poor, it appeared that fluorination of large quantities of U_3O_8 , with or without fluid beds, would require considerable development work on heat transfer and reaction-control techniques before the processing scheme could be reduced to a dependable status.

G. Removal of UO_2 Pellets from Cladding Materials

The combined decladding and fluorination steps (i.e., chemical de-jacketing of fuel elements followed by fluorination to UF_6) in the fluidized bed fluoride volatility process were briefly investigated in the pilot-plant development work. Zircaloy-2 and stainless steel were considered as the types of cladding material generally used in conjunction with the low-enrichment fuels.

For simulated fuel elements clad in Zircaloy-2, the greatest emphasis on chemical decladding was placed on experiments with HF-10% HCl gas mixtures which are particularly effective in promoting chemical attack of zirconium alloys.¹⁴ The decladding reaction occurs by conversion of the Zircaloy to solid zirconium tetrafluoride. The reaction of the cladding was aided by the action of the fluidized bed, and uranium dioxide pellets were not attacked by the gas mixture. A test was also made of the decladding of the Zircaloy-2 by direct reaction with fluorine.

For simulated fuel elements clad in stainless steel, actual chemical removal of the cladding was not attempted; the experimental approach was to remove the UO_2 from clad segments which were mechanically broached. Removal of UO_2 from the cladding was accomplished by oxidizing the fuel to U_3O_8 powder, which is significantly less dense than UO_2 . The expansion of the U_3O_8 material was often sufficient to split the cladding, thereby effecting removal of the uranium oxides from the cladding interior. The feasibility of this method of UO_2 separation was demonstrated in laboratory studies wherein the clad UO_2 was exposed to oxygen by means of punched holes¹⁵ or milled slots¹⁶ in the cladding. Oxidation of the UO_2 to U_3O_8 ruptured the cladding and permitted complete removal of the uranium. Oxidative separation studies have also been carried out with short segments (0.94 in. long) in a fluidized-packed-bed reactor.¹⁷ These studies demonstrated that about 95% of the UO_2 could be removed from the stainless steel.

In the pilot-plant experiments reported here, emphasis was placed on the combined oxidation and fluorination of UO_2 from stainless steel. These experiments used short segments (approximately 1 in. long) to simulate sheared fuel rods and also longer segments (10 and 12 in. long) to simulate fuel rods that had been mechanically slit or perforated.

1. Chemical Decladding of Simulated Fuel Rods Clad in Zircaloy-2

The series of runs with pellets clad in Zircaloy-2 tubing is summarized in Table 13. Several processing parameters were studied: the chemical reactants, the fluid-bed material, the preprocessing of the clad segments (i.e., clad segments 14 in. long and simulated, chopped segments 1 in. long were used), and the mode of reactor operation.

TABLE 13. Decladding of UO₂ Pellets in Zircaloy-2 Tubing

Reaction Temperature: 500°C
 Superficial Gas Velocity: 0.5 ft/sec
 Zircaloy-2 Tubing: 0.030-in. wall thickness

Run	F ₂ (%)	N ₂ (%)	HF (%)	HCl (%)	Fuel-element Sections		Inert Fluid- bed Material	Observations
					A (%)	Length (in.)	Quantity Charged	
13	58	-	-	-	42	(a)	5	MgF ₂ Fluorination of Zircaloy with fluorine not any better than reaction with HF-10% HCl.
15	-	-	90	10	-	14	14	Fluorspar Reaction developed high ΔP across reactor.
17	-	-	90	10	-	14	7	Fluorspar Cladding destroyed; high ΔP did not develop.
18	-	-	90	10	-	14	10	Fluorspar Temperature excursion terminated run.
19A	-	-	90	10	-	14	10	Fluorspar Complete process-cycle attempt. Fluorspar caked upon exposure to fluorine.
19B	20	80	-	-	-			
21A	-	-	90	10	-	14	5	CaF ₂ ^d Complete process cycle. Decladding successful; temperature excursions during fluorination.
21B	20	80	-	-	-			
40 ^b	80	20	-	-	-	1	6-in. bed ^c	Al ₂ O ₃ Fluorination of simulated chopped fuel rods--high ΔP developed when reaction was 60% completed.
41 ^b	80	20	-	-	-	1	6-in. bed ^c	None Run similar to Run 40. Zirconium oxides and fluorides filled voids in bed; temperature excursions resulted.

^aFour Zircaloy coupons and a piece of Zircaloy tubing (1¼ in. long x 1/2 in. in OD).

^bRecycled gas consisting mainly of fluorine with nitrogen and some oxygen.

^cPacked-bed height.

^dReagent-grade CaF₂.

After exposure to fluorine the weight gain of four Zircaloy-2 coupons used in Run 13 ranged from 0.5 to 1.4%, while that of a tubing specimen was 4.2%. These results indicated that reaction of Zircaloy with fluorine, even when aided by the action of the fluidized bed, was less than would be expected by use of the HF-10% HCl gas mixture.

When HF-10% HCl was used to declad 14-in.-long, simulated fuel rod segments (see Run 15), a high pressure drop across the reactor developed. This was attributed to the fact that the segments occupied too much of the reactor cross-sectional area (55%) to allow good fluidization for the entire run. When the fuel-rod segments covered only 28% of the cross-sectional area (see Run 17), no excessive pressure drop was encountered. In Runs 15 and 17, removal of the Zircaloy-2 was essentially complete except for a few fragile sections of tubing. The pellets had remained intact during the decladding, and it was apparent that subsequent pellet fluorination would not be inhibited by the presence of cladding remnants.

Runs 18, 19, and 21 were intended to demonstrate the Zircaloy-2 decladding followed by in situ fluorination of the UO_2 pellets. Run 18 was prematurely terminated because of temperature excursions in the reactor; the excursions caused by local ignition of the Zircaloy could not be controlled because the temperature of the reactor was maintained at a high level, 500°C . In Runs 19 and 21, decladding of the Zircaloy was successfully demonstrated. However, in Run 29 caking of the CaF_2 bed material occurred; the caking was attributed to the reaction of fluorine with impurities in the fluorspar. In Run 21, which utilized reagent-grade CaF_2 , temperature excursions encountered during the fluorination limited the rate of UF_6 production to $4.5 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$.

In Runs 40 and 41, 6-in.-deep beds of 1-in.-long fuel segments of Zircaloy-clad UO_2 were used. The short segments which simulated mechanically chopped fuel rods were open at both ends for exposure of the UO_2 pellets to the enriched fluorine atmosphere (recycled process gas). Run 40 was carried out with a fluidized bed of alumina, whereas Run 41 was carried out without a fluid bed. In both runs, ignition of the Zircaloy caused rapid temperature excursions. The results of these excursions were sintering of the alumina bed material in Run 40 and sintering of the packed bed in Run 41. Thus it appeared that prior removal of the Zircaloy was required to avoid temperature excursions during fluorination of the pellets.

2. Removal of UO_2 from Mechanically Broached 304 Stainless Steel

a. Short Lengths of Simulated, Chopped Fuel Rods

For runs with short segments of simulated fuel rods, the general operating procedure involved a two-step process for the removal of UO_2 from Type 304 stainless steel. The initial step was a two-zone oxidation-fluorination treatment of the fuel material. In this step, oxidation of the UO_2 to U_3O_8 occurs in a lower, oxidation zone of the reactor (fluidized-packed bed) and fluorination of the U_3O_8 to UF_6 occurs in an upper fluorination zone (unhindered fluidized bed). The two-zone oxidation-fluorination was then followed in the second step by a separate operating period in which the

uranium remaining in the stainless tubing was exposed to fluorine (direct fluorination). Reactor effluent gases were recycled during this step to provide high concentrations of fluorine and to keep fluorine losses to a minimum. In one case, Run 74, direct fluorination of the charge was used instead of the two-step procedure. During this run, oxygen was fed into the reactor up to a maximum concentration of 29%. The operating conditions for runs which used short segments of fuel rods are given in Table 14.

TABLE 14 Operating Conditions for Fluid-bed Oxidation-Fluorinations with Short Segments of Simulated Fuel Rods

		304 SS Clad UO ₂ Pellets				
		Segment Length 0.94 in				
		UO ₂ Pellets/Segment 2				
		UO ₂ Pellets 0.42-in dia x 0.42-in cylinders				
		Fluid Bed Fused α -alumina ^a				
		Fluidizing Gas Nitrogen				
		Pulsing Conditions 2 pulses/min at 20 psig ^b				
		Run	71	72	74 ^c	75
<u>Materials Charged</u>						
UO ₂ Pellets	(g)		1224	3484	1710	1704
304 SS	(g)		55	287	275	274
Cladding Thickness	(mil)		10	10	20	20
Packed-bed Height	(in)		1.5 ^d	6	3	3
Al ₂ O ₃	(g)		7100	7087	6800	6100
Al ₂ O ₃ Size Limits	(mesh)		-40 +170	-40 +170	-40 +170	-40 +170
<u>Oxidation-Fluorination (Two-zone Operation)</u>						
Oxidation Zone	Temp	(°C)	450	450	-	400 ^e
	O ₂	(%)	22	22	-	88
	Gas Rate ^f	(cfm)	1.1	1.1	-	0.3
Fluorination Zone	Temp	(°C)	500	500	-	500
	F ₂	(%)	4-10	4-10	-	3-14
	F ₂ -Feed Diluent ^g	(cfm)	0.25	0.25	-	0.65
	Total Gas	(cfm)	1.4	1.5	-	1.0
Processing Time	(hr)		5.25	6.75		12.0
<u>Fluorination (Single-zone Operation with Recycled Effluent Gas)</u>						
Temp	(°C)		500	500	500	500
F ₂	(%)		58	25	9-42	64
O ₂	(%)		-	-	0-29	
Total Gas	(cfm)		0.6	0.6	0.7-1.2	0.7
Processing Time	(hr)		3.25	6.75	6.5	5.0
Total Processing Time	(hr)		8.5	13.5	6.5	17.0

^aBlue Label Alundum

^bIn Runs 72 and 74 manifold pressures of 30 and 40 psig were also used

^cTwo-zone step was omitted

^dSingle segments 1.4, 1.8, 6, and 12 in. long were also included. The tubing of the 6- and 12-in. segments was slit longitudinally

^eTemperature was raised to 500°C for the last 3.5 hr

^fAll gas rates are at 25°C and 1 atm

^gRecycled reactor effluent gas

The depth of the fluidized-packed bed was varied from 1.5 to 6 in. in these runs. In general, the packed section consisted of simulated fuel rod segments which were 0.94 in. long, open at both ends, and contained two pellets each. In Run 71, single segments, 1.4, 1.8, 6, and 12 in. long, were also included in the charge. The 1.4- and 1.8-in. segments contained 3 and 4 pellets, respectively. The tubing segments 6- and 12-in. long were mechanically slit along the length of the tubing. Typical specimens of segments used in the runs are shown in Fig. 21.

108-6163

Fig. 21. Typical Specimens of Type 304 Stainless Steel-clad Uranium Dioxide Fuel Segments

Typical specimens of the stainless steel-cladding residues from Run 71 are shown in Fig. 22. The uranium was entirely removed from

Fig. 22. Appearance of Typical Stainless Steel-cladding Residues from Run 71

the cladding during this run; 90% of the uranium was collected as the hexafluoride during the two-zone operation, and the remaining 10% during the direct fluorination. The smaller pieces of stainless steel cladding were recovered from the reactor in virtually the same form as charged; however, only small, thin fragments of the slit, longer segments of cladding were recovered. These fragments were about 1 sq in. in area and 0.003 in. thick. All of the stainless cladding segments had undergone fluorine attack, as was evident from formation of surface scale. The reasons for more severe attack of the longer segments is not known. These segments may have been carried upward out of the oxidation zone when the enclosed UO_2 was pulverized to U_3O_8 ; hence, the longer segments may have been exposed to a fluorinating environment for a longer period of time than the shorter segments.

In those cases in which the UO_2 was not entirely removed from the cladding, the pellet residues took the shape of the specimens

108-6161

Fig. 23. Uranium Dioxide Pellet Residues with Cladding Removed, Run 72

shown in Fig. 23, taken from the reactor following Run 72 and believed to be unconverted UO_2 . These residues indicated that the initial attack of the pellets occurred at the ends of the clad segments and that the subsequent attack hollowed out the pellet center. In this particular case, incomplete conversion of the dioxide may have been caused by excessive cooling of the fluidized-packed bed when larger quantities of nitrogen were introduced to the reactor due to an increased pulsing pressure (see Table 14). In Run 72, 67% of the original uranium was collected as the hexafluoride during the two-zone operation and 28% by direct fluorination, for an overall uranium removal of 95%.

The distribution of uranium dioxide as a function of packed-bed height is given in Table 15. These results were obtained in Run 75 after 12 hr of two-zone operation with a 3-in.-deep fluidized-packed bed. Uranium removal from the cladding was greatest in the upper third and less in the lower portions of the packed bed. This effect of position on the removal of uranium from cladding is attributed to the action of the gas pulse, which imparts greater movement to the uppermost sections of the bed, thereby aiding the removal of loose material from the clad segments that are located in the upper parts of the packed bed. Similar results were obtained in the oxidative decladding experiments which also used pulsed, fluidized-packed beds.¹⁷

TABLE 15. Uranium Dioxide Distribution in
Stainless Steel-clad Fuel Segments after
Two-zone Oxidation-Fluorination, Run 75

Operating Conditions: See Table 14
Processing Time: 12 hr

Fixed-bed Position	Upper	Middle	Bottom	Composite
Number of fuel segments	28	28	29	85
Initial UO_2 in segments (g)	561	561	582	1704
Approximate weight UO_2 after processing (g)	41	67	115	223
Indicated UO_2 removal (%)	93	88	80	87

The residue of uranium oxide in the cladding tubes from Run 75 appeared to be loosely packed U_3O_8 . About 87% of the uranium charge had been removed from the cladding in the 12 hr of two-zone operation. The cladding tubes were recharged to the reactor for an additional 5 hr of processing by direct fluorination (see Table 14); after this step was completed, 0.4 g of uranium compounds remained in the cladding tubes, for an overall uranium removal greater than 99.9%.

Direct fluorination of a 3-in.-deep bed of fuel-rod segments was carried out in Run 74. During the course of the run, the concentrations of oxygen and fluorine and the manifold pressure of the pulse nitrogen gas were increased (see Table 14) in order to increase the production rate of UF_6 . No experimental difficulties were encountered. However, because of low hexafluoride production rates [average of 6 lb UF_6 /(hr)(sq ft)] and a low fluorine efficiency (38%), the run was voluntarily terminated without attempting to remove uranium completely from the cladding. In comparison with the two-zone processing step, a production rate of 35 lb UF_6 /(hr)(sq ft) was obtained after 4 hr of operation in Run 75, whereas the rates in Run 74 were less than 8 lb UF_6 /(hr)(sq ft) in 4 hr of processing. After 6.5 hr of processing in Run 74, 59% of the original uranium charge had been removed from the cladding tubes.

The results of the fluid-bed oxidation-fluorination experiments with short segments of simulated UO_2 fuel rods clad in stainless steel are summarized in Table 16. The runs are compared on the basis of packed-bed height, UF_6 production rates, fluorine efficiencies, and processing times.

TABLE 16 Results of Fluid-bed Oxidation-Fluorination Experiments
with 0.94-in Segments of Simulated UO_2 Fuel Rods
Clad in Stainless Steel

Run		71	72	74	75
Packed-bed Height	(in)	15	6	3	3
Two-zone Oxidation-Fluorination					
Production Rates	[lb UF_6 /(hr)(sq ft)]	12	20	(a)	7
Fluorine Utilization ^b	(%)	38	61	(a)	58
Processing Time	(hr)	5.25	6.75	0	12.0
Direct Fluorination					
Production Rates	[lb UF_6 /(hr)(sq ft)]	2	8	6	3
Fluorine Utilization	(%)	7	37	38	16
Processing Time	(hr)	3.25	6.75	6.5	5.0
Overall Production Rates	[lb UF_6 /(hr)(sq ft)]	9	14	6	6
Overall Fluorine Utilization	(%)	27	51	38	42
Total Processing Time	(hr)	8.5	13.5	6.5	17.0
UO_2 Removed from Cladding	(%)	100	95	59	100

^aTwo-zone step was omitted

^bFluorine utilization = $3 \times \text{moles } \text{UF}_6 \text{ produced} / \text{moles } \text{F}_2 \text{ fed}$

In order to compare the individual runs, it should be pointed out that Run 75 differed from the other runs in several respects. First, a high concentration of oxygen (88%; see Table 14) was used for the oxidation. Secondly, the fuel segments were removed from the reactor following the completion of the two-zone processing to determine the extent of UO_2 removal. The segments were then recharged to the reactor for the fluorination step. The handling of the fuel segments may have influenced overall uranium removal; therefore, the complete removal of the uranium in this run is not directly comparable to in situ fluorination of the fuel segments. Thirdly, mechanical difficulties with the scale on the UF_6 condenser developed after 6.5 hr of two-zone processing; these difficulties prevented the measurement of UF_6 collection during the latter 5.5 hr of two-zone processing, thereby extending the processing time for this step. In the initial 6.5 hr of two-zone processing, 75% of the original uranium was collected as the hexafluoride at an average production rate of 15 lb UF_6 /(hr)(sq ft) and a fluorine utilization of 72%.

Although the results listed in Table 16 are not conclusive, it appears that uranium can be completely removed from clad segments of chopped fuel elements by suitable reaction with oxygen and fluorine in a fluidized-packed bed system. These results also indicate that a two-step procedure of two-zone oxidation-fluorination followed by a direct fluorination cleanup step is preferable to a single-step procedure of direct fluorination. For conditions of complete uranium removal, the problems of maximum allowable packed-bed height, minimum processing time, and the extent of

fluorination of the stainless steel require further investigation. Extensive fluorination of the stainless steel is not desirable because this reaction would result in the formation of volatile chromium fluorides which would be collected as a contaminant in the UF_6 product.

b. Simulated Fuel-rod Bundles

The two-zone method of oxidation and fluorination was also applied to the removal of UO_2 from segments of simulated fuel rods 10 and 12 in. long. The stainless steel cladding on these segments was either slit or perforated longitudinally. The segments were then charged to the reactor as a vertical bundle of fuel rods. For Run 73, a continuous slit along the length of the 10-mil-thick 304 stainless steel cladding was made by means of a 1/16-in.-wide carborundum grinding wheel. A typical specimen of the slit segments was shown in Fig. 21. For Run 76, stainless steel tubes, of 20-mil wall thickness and packed with UO_2 pellets, were perforated the entire length of the tubing by a spiked wheel device. The holes were 1/16 in. wide by 3/16 in. long by 3/32 in. deep and were spaced approximately 11/32 in. between centers (see Fig. 24). The operation conditions used to process the bundles of simulated fuel rods are given in Table 17.

When the bundle of fuel rods with slit cladding was processed in Run 73, virtually all of the uranium charge was converted to UF_6 in the 9.5 hr of two-zone oxidation-fluorination. The fluorine utilization, based on hexafluoride conversion, was 55.4%, and the average production rate was 18 lb UF_6 /(hr)(sq ft). The cladding tubes were then removed from the reactor prior to the fluorination for cleanup of the alumina bed. This cleanup step reduced the uranium concentration in the alumina from 0.28 to 0.08 w/o. As a result of the inclusion of the cleanup fluorination, the overall fluorine utilization for the run was reduced to 38%.

In Run 76, the bundle of simulated fuel-rod segments consisted of UO_2 pellets encased in 11.6-in. lengths of 0.020-in.-thick Type 304 stainless steel tubing which had been perforated by the spiked wheel device. For the two-zone processing step, an oxygen concentration of 88% was used. This concentration was higher by about a factor of four than that used in Run 73. In Run 76, the UO_2 was completely removed from the cladding in 7.5 hr of two-zone oxidation and fluorination. After this processing step the cladding was removed from the reactor; the cladding had been completely split open by the oxidation of UO_2 to U_3O_8 . The cladding specimens are shown in Fig. 24. On some of the tubes there was a metal fluoride film which indicated corrosive attack by fluorine during the run. Since these tubing pieces were located below the point of introduction of fluorine, the corrosive attack may have occurred by diffusion or back-mixing of fluorine into the oxidation zone.

108-6607A

Fig. 24. Cladding Tubes Ruptured by the Oxidation of UO_2 to U_3O_8 during Run 76

TABLE 17. Operating Conditions for Fluid-bed Oxidation-Fluorination Experiments with Simulated Fuel Rods Which Were Mechanically Slit or Perforated

UO₂ Pellets: 0.42-in. dia x 0.42-in. cylinders
 Fluid Bed: Fused α -alumina
 Fluidizing Gas: Nitrogen
 Pulsing Conditions: 2 pulses/min at 20 psig

	Run	73	76
<u>Materials Charged</u>			
UO ₂ Pellets	(g)	2886	3249
304 SS Cladding	(g)	204	497
Thickness	(mil)	10	20
Segment Length	(in.)	10.3	11.6
UO ₂ Pellets per Segment	-	24	27
Number of Segments	-	12	12
Cladding Treatment	-	Slit	Perforated
Al ₂ O ₃ :	(g)	7100	6100 ^a
Size Limits	(mesh)	-40 +170	-80 +200
<u>Oxidation-Fluorination (Two-zone Operation)</u>			
Oxidation Zone: Temp	(°C)	450 ^b	475
O ₂	(%)	7-23	88
Gas Rate	(cfm) ^c	1.1	0.3
Fluorination Zone: Temp	(°C)	500	475
F ₂	(%)	5-10	9-24
F ₂ -Feed Diluent ^d	(cfm)	0.25	0.65
Gas Rate	(cfm)	1.5	1.0
Processing Time:	(hr)	9.5	7.5
<u>Fluorination (Single-zone Operation with Recycled Effluent Gas)</u>			
Temp	(°C)	500	500
F ₂	(%)	90	68-83
Gas Rate	(cfm)	0.8	0.65
Processing Time:	(hr)	4.4	10
<u>Total Processing Time</u>	(hr)	13.9	17.5

^aAlumina bed was also used for Run 75.

^bTemperature was raised to 500°C for the last 4.0 hr.

^cAll gas rates are at 25°C and 1 atm.

^dRecycled reactor effluent gas.

The UF₆ production rates observed in Run 76 were quite uniform, more so than might have been expected for a process which depends on the rupture of stainless steel cladding. The bar graph in Fig. 25 indicates the degree of uniformity in the UF₆ production rate. For the first 6 hr of operation, the UF₆ production rates averaged 30 lb UF₆/(hr)(sq ft). At this point in the run, 96% of the uranium charge had been collected as UF₆ at a fluorine utilization of 88%. The overall fluorine utilization for the 7.5 hr of two-zone processing was 72%. The average rate of UF₆ production and the overall fluorine utilization obtained in this run were the highest obtained in the processing of clad UO₂ pellets by the two-zone oxidation-fluorination technique.

108-7266

Fig. 25. Uranium Hexafluoride Production Rates in Run 76

times thicker if the slits in the cladding were sufficiently extensive. A continuous longitudinal slit effectively destroys the physical integrity of the cladding and exposes large portions of the pellet surface area to reaction with oxygen. However, as was shown in Run 76, it appears that adequate exposure of the pellets to oxygen can be achieved through perforations in the cladding. In this run, the perforated, 20-mil-thick stainless steel tubing was ruptured by oxidation of the contained UO_2 pellets. The pulverized pellets were completely removed from the cladding tubes without the use of external mechanical attachments for vibration of the cladding and without exposure of the cladding to a fluorine cleanup step. However, additional fluorination of the alumina in the fluid bed was required to recover all of the uranium as UF_6 . The alumina bed from Run 76 (which was also used in Run 75) was subjected to a cleanup fluorination: after 10 hr of additional fluorination, the uranium concentration in the final bed was 0.035 w/o. It therefore appears that virtually complete removal of uranium from the alumina can be achieved by the cleanup with fluorine.

H. Fluorination of Deep Beds of UO_2 Pellets

In order to evaluate the effect of process variables with the greatest economy of time and reagents, earlier work with the fluorination reaction concerned the processing of shallow pellet beds with depths of 3 to 9 in. Practical processing conditions would require the fluorination of deeper beds of pellets. One reference depth for the deep-bed runs is that corresponding to the maximum amount of UO_2 pellets which would be put into the column in the form of 30-in. fuel rods (before decladding); the number of rods would be limited to approximately 25% of the cross-sectional area of the column in order to ensure adequate fluidized solids mixing and gas

In both Runs 73 and 76, the uranium was completely removed from cladding by the two-zone oxidation-fluorination process; hence, a final direct fluorination (i.e., single-zone operation) was needed only to effect a cleanup of the alumina bed and not to complete the removal of UO_2 from the cladding as was necessary in the runs made with short fuel segments. Although the uranium was removed from slit cladding with a wall thickness of only 0.010 in., it is believed that uranium removal would also be complete from cladding several

contacting. With this area limitation, the amount of pellets contained in these fuel rods would correspond to a pellet-bed depth of approximately 18 in. (a batch charge of 29.0 lb). This quantity of pellets was therefore used for a series of six deep-bed fluorination experiments.

1. Operating Conditions

Three systems of gas flow were investigated with the intent to maximize fluorine utilization. These systems included once-through gas flow, maximum off-gas recycle, and partial recycle of the off-gas (see Fig. 10). With each gas-flow system, fluorine was added to the gas stream to compensate for fluorine consumption by reaction. Fluorine feed to the column was controlled by temperature difference between the fluidized-packed bed and the operating temperature (500°C).

Fluorine utilization in the reactor was dependent upon the rate of off-gas recycle relative to gas throughput. Since oxygen in the recycled gas reacted with the pellets to form U_3O_8 fines, the recycle rate was limited by the amount of oxygen in the gas. As rates of UF_6 production increased, oxygen content of the recycled gas also increased while fluorine concentration decreased, and the recycled gas essentially contributed to fines formation in the column rather than to increased UF_6 production rates.

Nominal operating conditions for the series of deep-bed pellet-fluorination experiments are shown in Table 18. Significant variations in

TABLE 18 Nominal Fluorination Conditions for Deep Beds of UO_2 Pellets

		UO_2 Pellets Pellet Bed Height Weight Al_2O_3 Size Limits					
		H_2 fired 0.5-in dia x 0.5 in cylinders 18 in 29 lb -60 +200 mesh					
	Run	49	50	52	53	54	55
Reaction Temperature	(°C)	450	450	490	500	500	500
Pellet-bed Support		plate	plate	plate	plate	Ni balls	Ni balls
Height of Pellet Support above Flange ^a	(in)	7	14	14	4	4	4
<u>Gas Flow</u>							
System ^b	-	A	B	B	C	C	C
Velocity minimum	(ft/sec) ^c	0.5	0.5	0.6	1.0	0.9	1.0
<u>Maximum Reactant Concentration^d</u>							
O_2	(%)	1.4	7.0	6.6	6.5	3.9	1.1
F_2	(%)	24.3	32.0	30.0	22.5	12.2	9.0
<u>Fluidized Alumina Bed</u>							
Weight	(lb)	3.5	8.4	8.4	7.3	7.3	4.4
Static Height above Pellets	(in)	-9 ^e	9 ^e	-9 ^e	3	3	-5 ^e
Al_2O_3/UO_2	(lb/lb)	0.12	0.29	0.29	0.25	0.25	0.15
Total Processing Time	(hr)	4	29	31.2	22.3	43.5	26
Conversion of UO_2 Charge to UF_6	(%)	6	94	~100	96	99	73

^aReference height is the bottom flange of reactor, conical gas distributor was 2-3/4 in high

^bThe systems used for gas flow through the reactor were A--maximum off-gas cycle, B--no recycle, C--partial recycle

^cBased on empty-column cross-sectional area and control temperature

^dGas entering fluidized-packed bed

^eStatic bed was below top of pellets

physical and chemical variables occurred from run to run, and the effect of each change of variable was difficult to interpret for each run. The changes effected during each run were based on experience gained as the series of runs progressed and were made with the primary intention of maximizing fluorine utilization and the rate of UF_6 production. Good fluidization quality was a requisite for the final evaluation of the process variables.

The effect of the height of the pellet-support plate in the column was observed in Run 49. Before fluorination was started, a temperature profile in the fluidized-packed bed showed that the temperature of the bottom of the bed was 200°C less than that at a point 6 in. above the bottom, whereas temperatures in the upper 12 in. of bed were uniform. This temperature difference was attributed to heat losses through the bottom flange of the reactor. For subsequent runs, uniform bed temperatures were obtained by heating the bottom flange of the reactor.

The $\text{Al}_2\text{O}_3/\text{UO}_2$ weight ratio (approximately 0.25) used in the deep-bed runs was less by a factor of about 10 than those used in previous fluorinations. In all cases however, the expanded height of the fluidized alumina was sufficient to cover the top layer of pellets in the 18-in.-deep bed. For the deep-bed runs, the weight ratio of alumina to UO_2 was based on data from concurrent laboratory studies⁹ which indicated that some plutonium would be retained in the alumina bed after fluorination.

Of the variables shown in Table 18, the gas-flow cycle had the most significant effect upon the fluorination. With single-pass gas flow (no recycle), fluorine and oxygen concentrations were controlled from the panel board. With maximum off-gas recycle, the rate of UF_6 production influenced oxygen and fluorine concentrations in the recycled gas. Some oxygen was desirable to promote U_3O_8 fines formation and thereby increase the fluorine efficiency; however, control of the oxygen concentration was difficult with the system on maximum recycle. Control of oxygen in the recycled gas was facilitated by recycling a portion of the reactor effluent gas and by diluting the recycled gas with nitrogen. With this modification, it became possible to utilize recycled off-gas for the purpose of increasing fluorine utilization. A mathematical model relating the fluorination reaction to several process variables including off-gas recycle conditions was derived to assist in the interpretation of experimental results. This analysis is given in the Appendix.

2. Single-pass Gas Flow--Runs 50 and 52

The feasibility of processing deep beds of pellets was established in two runs using single-pass gas flow for the major part of the fluorination. These runs were carried out under similar conditions and differed mainly in the operational procedure employed during the early part of the run.

In Run 50, fluorine was introduced through a side port in the reactor to the upper 6.5 in. of the fluidized-packed bed, and oxygen (in nitrogen) was fed to the bottom of the reactor. Approximately 25% of the UO_2 charge was fluorinated to UF_6 in this manner; the run was completed with fluorine fed to the bottom. Shortly after the change in fluorine feed point was made, an unscheduled shut-off of the fluorine occurred. Oxygen feed was continued for a period of about an hour before the fluorine shut-off was detected; consequently, a buildup of U_3O_8 fines occurred, and a partial caking condition developed when fluorine flow was resumed.

About 1 lb of caked material was found in the reactor after the run. The caking (which was attributed to the fluorine shut-off) and the low fluorine utilization (33%) were regarded as the only unsatisfactory aspects of the run. The run was considered to be a successful demonstration of deep-bed processing since 94% of the UO_2 charge was recovered as UF_6 product, and during the latter 2/3 of the run, acceptable production rates of 50 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$ were maintained with good fluidization quality.

In Run 52, oxygen was used during half of the fluorination period, and for a major portion of the run, fluorine feed rates were maintained at 25 to 30% of the total gas flow.

Fig. 26. Uranium Hexafluoride Production Rates in Run 52

The periods of oxygen feed are shown in Fig. 26. The effect of oxygen on the production rate is shown in the figure; in particular, during the 7th hour of operation the rate of production increased to 45 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$ after a short period of oxygen feed. When oxygen was shut off, the rate dropped to 22 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$; a resumption of oxygen feed increased the rate to 35 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$.

When 80% of the pellet charge had been reacted, the system was put on recycle; however, fines formation was encountered after 2 hr. A sample of the alumina bed taken during the recycle period contained 6% U. This result indicated that oxygen concentration in the recycled gas had built up to high levels. In the final portion of the run the fluorination was carried out with single-pass gas flow.

The uranium was completely removed from the reactor during the run under conditions of satisfactory temperature control at $490 \pm 10^\circ\text{C}$ and with a complete absence of caking problems. The overall fluorine utilization was low (29.4%), probably resulting from the rather constant rate of fluorine feed, which did not match closely the rate of UF_6 production.

At comparable periods of processing time, production rates for Run 52 were higher than those for Run 50. In Run 52, production rates were higher than 27 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$ during the first two-thirds of the run, whereas during Run 50, the high production rate period did not occur until the latter part of the run. A comparison of the UF_6 production rates for both runs is shown in

Fig. 27. Comparison of Uranium Hexafluoride Production in Two Deep-bed Uranium Dioxide Pellet-fluorination Runs

for both runs is shown in Fig. 27. The generally higher and more uniform UF_6 production rate in Run 52 was due to a slightly higher and more uniform operating temperature, with a consequent uniform rate of fluorine introduction.

The results from Runs 50 and 52 with once-through gas flow indicated that fluorination of deep beds of pellets could be achieved with good fluidization quality and temperature control at fair overall production rates of about 25 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$. The results also indicated that

close control of oxygen was important if stable operating conditions and freedom from caking were to be maintained. Fluorine utilization in these runs was not satisfactory; consequently, off-gas recycle was used in other runs in an effort to increase fluorine utilization.

3. Recycled Gas--Runs 49, 53, 54, and 55

In a preliminary run with off-gas recycle, Run 49, the process off-gas was recycled in a manner similar to previous runs with 6-in.-deep fluidized-packed beds, i.e., fluorine was the only gas admitted to the recycle system. Also, the inventory of alumina was low for the run ($\text{Al}_2\text{O}_3/\text{UO}_2 = 0.12$, see Table 18) because it was believed that good heat transfer could be maintained with a minimum of alumina. Longitudinal temperature profiles showed uniform temperatures in the top 12 in. of the pellet bed; however, the lower 6 in. were 200°C cooler. This temperature difference was attributed to heat losses through the bottom flange of the reactor. With this temperature difference and with uncontrolled oxygen buildup in the recycle gas (due to UF_6 production), severe caking of the bed developed after 4 hr of operation. Although the large temperature gradient across the fluidized-packed bed and the low inventory of alumina may have contributed to this result, the cause of the caking was attributed to a lack of control over oxygen concentration in the recycle gas; consequently, in subsequent runs (Runs 53, 54, and 55), the recycle scheme was modified according to

the mathematical model (see Appendix) by the addition of nitrogen feed to the system. In addition, the bottom flange of the reactor was heated and insulated and, with the exception of Run 55, the alumina inventory was increased to a $\text{Al}_2\text{O}_3/\text{UO}_2$ ratio of about 0.3 (see Table 18).

The use of a modified recycle scheme permitted some control over the quantity of oxygen entering the fluidized-packed bed. In particular, it was believed that the most important variable was the mole ratio of F_2/O_2 entering the reactor. From the stoichiometry of the reactions involved it appeared that this ratio should be maintained near nine. This ratio is based on the following equations:

The F_2/O_2 ratio was actually varied widely during runs with and without gas recycle, as shown in Table 19.

TABLE 19. Summary of Stable Operating Periods during Fluorination of 18-in. Uranium Dioxide Pellet Beds

Run	Process Time (hr)	Approx Height of Pellets Remaining (in.)	Off-gas Recycle Rate (cfm) ^a	Fluidization Velocity (ft/sec) ^b	Nitrogen Dilution ^c (b/a)	Recycle Ratio ^d (c/a)	Reactor Inlet			UF ₆ in Off-gas (%)	UF ₆ Production [lb/(hr)(sq ft)]	F ₂ Utilization for Run Period (%)	Comments
							F ₂ (%)	O ₂ (%)	(F ₂ /O ₂)				
50	20-26	8-2	0	0.8	2.9	0	25.5	0	-	3.8	42	49	
52	2.5-6.5	17.5-14.5	0	0.8	2.9	0	25.6	0	-	1.9	20	21	Good fluidization and heat transfer.
	8.1-13.2	13-10	0	1.0	2.0	0	32.0	2.5	12.8	2.6	31	23	Good fluidization and heat transfer.
	16.3-18.7	6.5-4.5	0	0.9	2.4	0	27.3	6.5	4.2	4.1	45	41	Good fluidization and heat transfer
	22-25.6	3-2	0.5	1.2	5.5	3.8	13.3	0.6	22.2	1.6	15	31	Temperature control difficult on recycle.
	26.4-29.2	2-1	0	0.7	8.3	0	10.7	0	-	1.5	13	42	
53	1-9	17.5-13.5	0.7	0.9	2.3	8.1	14.2	6.0	2.4	2.2	24	77	
	9-17.3	13-2	0.7	0.9	1.0	3.9	22.5	12.3	2.1	5.0	57	87	High production rates-- cake forms at end of period
	17.3-22.3	2-1	0.7	0.7	0.6	16.3	25.5	51.7	0.5	-	8	48	Additional caking encountered with O ₂ introduction.
54	1-12.5	18-11	0.8	1.0	3.3	0.9	12.2	3.9	3	1.7	21	70	Some caking developed.
	17-37	10-1.3	0.9	1.2	7.0	15.0	4.8	2.4	2	1.3	20	92	Good fluidization and heat transfer.
55	1-5	18-16	0.5	1.3	9.3	5.3	9.0	0.6	15	1.6	18	53	
	5-7	16-15	0.65	1.4	8.8	6.5	8.2	0.6	13.7	1.6	18	53	Decreasing bed pressure drop.
	8-13	15-12	0.65	1.4	8.7	6.9	8.0	1.1	7.3	2.6	26	76	
	16-21	11-8	0.5	1.2	10.3	6.6	6.1	1.0	6.1	2.4	23	85	
	21-25	8-5	0.5	1.2	10.0	6.4	8.3	1.0	7.5	3.0	28	78	Channeling in bed.

^aVolumetric gas rates at 1 atm and 25°C.

^bLinear gas rates at 1 atm and column conditions, based on total cross-sectional area of reactor.

^cNitrogen dilution factor - N₂ entering system, in moles per hour/F₂ entering system, in moles per hour (see Appendix)

^dRecycle gas ratio = recycle gas stream, in moles per hour/F₂ entering system, in moles per hour (see Appendix).

The data in Table 19 were taken from the most stable operating periods for the series of deep-bed runs. Stable operation was arbitrarily defined to occur in periods during which relatively constant gas-feed rates and UF_6 production rates were maintained without operational difficulties. Relatively constant gas rates (in particular fluorine feed rates) in these cases implied good fluidization and heat transfer in the fluidized-packed bed.

The inlet F_2/O_2 ratio did not correlate with hexafluoride production and fluorine utilization in a significant manner. Ratios above and below the stoichiometric equivalent of 9 were observed to provide periods of good heat transfer and fair production of UF_6 (see Table 19). However, the inlet F_2/O_2 ratio, which was operationally satisfactory in one run, proved to be inadequate as the run progressed or when used in a subsequent run (e.g., Run 54, periods 1-12.5 and 17-37 hr, and Run 55, period 5-7 hr). This behavior of the system was attributed to variations in the F_2/O_2 ratio within the bed due to variation in the rate of production of UF_6 . The formation of UF_6 released oxygen and consumed fluorine, thereby reducing the actual F_2/O_2 ratio in the fluidized-packed bed. Low F_2/O_2 ratios promoted fines formation by oxidation of the UO_2 to U_3O_8 and there was insufficient F_2 to produce UF_6 ; fines formation was further increased by UF_6 reaction with uranium oxides to form solid intermediate uranium fluorides. Fines transport from the fluidized-packed bed was apparently inadequate to prevent local hot spots from developing, which accelerated the chemical reactions and led to caking of the bed. This postulated mechanism for caking of the bed appeared to be a function of the rate of UF_6 production. In runs with

recycled gas, sustained production rates of about $20 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ appeared to be the maximum rate which could be maintained without operational difficulties.

Fig. 28. Uranium Hexafluoride Production during Run 53

The rates of production for UF_6 during Run 53 are shown in Fig. 28. The rates can be classified into three separate periods: a moderate production period with an average rate of $24 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ for the first 9 hr of operation, a high production period with an average rate of $57 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ for the next 8 hr of operation, and a low production period with an average rate of $8 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ for the final 5 hr of operation. The operating conditions for the run are given in Table 19 and Fig. 29.

Fig. 29. Average Nitrogen and Fluorine Feed Rates and Uranium Hexafluoride Production Rates, Run 53

Runs 54 and 55 were also carried out with the modified gas-recycle system; operating conditions for these runs were similar to Run 53 and are listed in Table 19.

Toward the end of the high-rate period during Run 53, a partial caking condition developed in the fluidized-packed bed; during this period the UF_6 concentration in the reactor off-gas averaged 5%, which was comparatively high. In Run 55, the UF_6 concentration in the off-gas was 1.6 to 3%, and in Run 54, 1.7% for the first part of the run and 1.3% for the last half of the run (which was operationally better than the first half). It appears that the small differences in UF_6 concentration may significantly affect operation of the system since during these periods the concentration of oxygen, which at high levels also affects the fluidization quality, was maintained at low levels. The differences in uranium hexafluoride concentration were due solely to differences in the rate of UF_6 production.

Through use of off-gas recycle (in Runs 53, 54, and 55), the fluorine utilization was improved by a factor of about 2 relative to runs with once-through gas flow (in Runs 50, 52). Overall fluorine utilization for the three partial recycle runs was 70 to 78%. However, in several periods of recycle operation, fluorine utilization was greater than 80%, e.g., Run 53, 87% for 8 hr; Run 54, 92% for 20 hr; and Run 55, 85% for 5 hr (see Table 19). The fluorine utilization depends largely upon several factors: (1) the fraction of the total gas throughput which is recycled, (2) the quantity of fines present in the reactor, and (3) the efficiency of contact between the fine particles and fluorine. Recycle of process off-gas provides a re-use of fluorine which would otherwise be wasted; the recycle stream also provides oxygen for fines formation which, together with the recirculated fluorine, tends to increase the fluorine utilization. However, since fluorination to volatile products is the only means of removing fine particles of uranium compounds from the reactor, the F_2/O_2 ratio in the reactor would appear to be particularly important. Although the partial-recycle scheme employed in Runs 53, 54, and 55 successfully limited oxygen concentrations in the reactor and retained some of the benefits of gas recycle, it did not provide

consistently good fluidization or eliminate caking tendencies. Caking was severe in Run 49 when oxygen concentration to the reactor was not controlled. With control of oxygen by means of the partial recycle scheme, less severe caking was encountered and temperature control was difficult only at high fluorination rates; however fluorination could be continued at lower rates as shown in Run 54.

4. Summary Evaluation of Deep-bed Runs

The major objective of the deep-bed runs was to obtain satisfactory performance simultaneously with respect to fluidization quality, fluorine utilization, and batch-processing time under practical operating conditions. Fluidization quality is taken to mean adequate fluidization of the alumina for the equalization of temperatures in the reaction zone and for the conduction of reaction heat to the cooling wall without large temperature differentials. These conditions imply efficient gas-solid contacting with no caking of solids or channeling of gas in the bed. A final criterion is that the bed consists of freely flowing inert solids at the end of the fluorination.

A comparison of the series of deep-bed runs in terms of the major objectives and standards of evaluation is given in Table 20. As shown, each run had a "poor" rating in at least one of three categories. In Runs 50 and 52, fluidization quality was good, but fluorine utilization was low and production rates were moderate. The attempt to maximize fluorine utilization by recycle of the off-gas with no control over oxygen concentration (as in Run 49) was not successful. With partial recycle and control over the oxygen to the reactor, good fluorine utilization was obtained (in Runs 53 and 54); however, fluorine economy and fluidization quality appeared promising under operating conditions for which production rates were below 20 lb UF₆/(hr)(sq ft) (see Run 54). These data suggest the possibility of a correlation between low fluidization quality (or caking) and the higher concentrations of UF₆ associated with higher production rates.

TABLE 20 Summary Evaluation of Six Deep-bed Fluorination Runs

Run	Control Temp (°C)	Charge Ratio Al ₂ O ₃ /UO ₂	Gas Recycle	Overall Estimate of Fluidization Quality (Rating)	Overall Fluorine Utilization		Overall Average UF ₆ Rate	
					(%)	(Rating)	[lb/(hr)(sq ft)]	(Rating)
49	450	0.12	Max Recycle· High O ₂	Poor	-	-	9	Poor
50	450	0.29	No	Good ^a	37	Poor	24	Fair
52	500	0.29	No; but some O ₂ added	Good	29	Poor	25	Fair
53	500	0.25	Partial Recycle	Poor	77	Good	32	Fair
54	500	0.25	Partial Recycle	Good ^a	78	Good	17	Undesirably Low
55	500	0.15	Partial Recycle	Poor	70	Fair	21 ^b	Low

^aBetter period was last part of run (see text and Table 19)

^bRun was terminated at 73% of complete fluorination.

I. Two-zone Oxidation-Fluorination of UO₂ Pellets

1. Gas-Solid Chemical Reactions

In the fluorination of uranium dioxide pellets, the heat of reaction¹¹ for the overall reaction is given by the equation

With separate oxidation and fluorination zones, the heat of reaction¹¹ may be divided because the overall reaction takes place in two steps:

and

Since heat transfer in the fluidized-packed bed is relatively poor compared to an unhindered fluidized bed,⁶ a significant advantage of the two-zone operation over single-zone fluorination is that oxidation, with a relatively low heat of reaction, takes place in the packed bed of pellets while fluorination, with a high heat of reaction, is carried out in the fluidized bed above the packed bed.

The mechanism of oxidation of the uranium dioxide is thought to be one of diffusion of oxygen to the tetragonal lattice U₃O₇ followed by a process of nucleation and growth of U₃O₇ to orthorhombic U₃O₈.^{13, 18, 19, 20} A 30% change in volume occurs with the phase change during oxidation with the result that the U₃O₈ tends to spall from the surface of the pellets; the spalling is aided by the turbulent motion of the fluid bed.

In the two-zone system, the powdered U₃O₈ must be physically transported to the fluorination zone in order for the fluorination to proceed. This process is shown schematically in Fig. 30. The transport of the oxide powder must be accomplished in a manner which prevents formation and accumulation of intermediate uranium fluorides. These intermediates are produced as fine powders by the following reactions:

Fluidized beds with large concentrations (above approximately 20%) of the intermediate uranium fluoride powders may be difficult to maintain in a

fluidized condition. Channeling and packing of fine particles with reduced heat transfer in the presence of the fluorine reactant can cause caking of the bed. Removal of fines in the fluid bed takes place according to equations 3, 7, and 10:

108-7608

Fig. 30. Schematic Diagram of Two-zone Oxidation-Fluorination of Uranium Dioxide Pellets

Therefore, the major requirements for practical hexafluoride production rates were the proper balancing of the oxidation and fluorination rates, and the control over the transport of U_3O_8 powder from the oxidation zone to the fluorination zone. Control of powder transport prevented accumulation of U_3O_8 fines in the oxidation zone, thereby reducing the possibility that large amounts of these powdered solids enter the fluorination zone. Rapid introduction of powders to the fluorination zone would result in intermediate uranium fluoride formation and elutriation of this powder to cooler parts of the reactor.

2. Control of Fines Transport from the Oxidation Zone

Several methods of promoting transport of fine powder were investigated: increased fluidization velocities, column vibration, and the use of gas pulses introduced to the fluidized-packed bed. In addition, a longitudinal (i.e., axial) temperature gradient was maintained in the pellet bed in some runs in an effort to promote preferential oxidation in the upper layers of the pellet charge. The experimental conditions and results for the two-zone runs are reported in Table 21 and are discussed below.

Accumulation of intermediate fluorides was avoided by maintaining a slight excess of fluorine in the off gas. Fluorine requirements were ascertained by monitoring uranium hexafluoride collection in the product condenser and the fluorine concentration in the reactor effluent stream.

In this system, the UF_6 production rate depends on the rate of oxidation and the rate of U_3O_8 transport to the fluorination zone, as well as fluorination rates.

TABLE 21. Two-zone Oxidation-Fluorination of UO₂ Pellets

UO ₂ Pellet Charge:	Weight:	19.4 lb
	Bed Height:	12 in.
Alumina Charge:	Weight:	11.9 to 17.8 lb
	Size Limits:	-40 +170 mesh
Oxygen Diluent:	N ₂	
Fluorine Diluent:	Runs 61-66:	None
	Runs 68-70:	Process off-gas
Fluorination Zone:	Temperature:	500-525°C
	Gas Rate:	1.1-1.6 cfm
	Fluorine:	7-17%

Run	Mode of Operation	Oxidation Zone			Processing Time (hr)	UO ₂ Reacted to UF ₆ (%)	Average Production Rate [lb UF ₆ /(hr)(sq ft)]	Average Fluorine Utilization ^a (%)
		Temp (°C)	Oxygen (%)	Gas Rate (cfm)				
61	Intermittent column vibration	500	3 to 8	1.4	15.5	88	32.0	58.6
62	Continuous column vibration	400	4 to 12.5	1.3	13.0	82	32.4	53.6
63	Thermal gradients ^b	≤ 400	18 to 31	1.1	13.8	95	35.6	49.0
64	Thermal gradients ^b	≤ 400	26	1.2	16.3(18.3) ^c	92(97) ^c	31.0	56.8(53.0) ^c
65	Pulsed gas and thermal gradients	400	22	1.3	13.5	46	17.6	49.5
66	Pulsed gas and thermal gradients	400	20	1.0	1.5	-	-	-
68	Pulsed gas, subcooled pellets	340-480	4.5	0.9	13.5(15.0) ^c	99(100) ^c	37.9	66.5(64.5) ^c
69	Pulsed gas, subcooled pellets	340-480	6	0.9	10.0(12.5) ^c	97(100) ^c	50.0	74.9(72.5) ^c
70	Pulsed gas, subcooled pellets	340-480	8	1.0	9.2(12.5) ^c	94(100) ^c	52.0	78.5(74.9) ^c

^aAverage fluorine utilization = 100 [3 x (moles UF₆ produced)/(moles F₂ fed)].

^bThe temperature of the UO₂ pellet bed was lower at the bottom, in order to promote oxidation preferentially near the upper surface of the bed.

^cValues given in parentheses are final results of two-zone processing plus an additional period of uranium cleanup in which 50 to 80% F₂ is recycled through the reactor at 500°C.

High gas rates aid fines transport from the oxidation zone but also tend to elutriate a portion of unreacted and partially fluorinated U_3O_8 fines from the fluorination zone even though an excess of fluorine is maintained. Most of the elutriated powder accumulates on the cone joining the column to the disengaging section, while the rest is collected by the metal filters. Reaction of U_3O_8 , UO_2F_2 , and UF_4 with fluorine in the upper parts of the column is slow because of the reduced temperature (200-300°C) in this region. In the runs described below, it was found that the major problem was to control the rate of entry of oxide fines to the fluorination zone.

The first run in the development program which utilized the two-zone oxidation-fluorination technique was Run 61; in this run high superficial fluidization velocities (1.2 to 1.4 ft/sec) were used. The effect of external column vibration was investigated during a 2.2-hr period. External vibration was applied to the reactor by means of an automatic hammer device which struck the reactor at a rate of 20 blows/min. During this period of operation, the external vibration increased the UF_6 production rate from 27 to 70 lb [$\text{UF}_6/(\text{hr})(\text{sq ft})$]; however, it was not evident whether the increased production rate caused by vibration was due to return of elutriated fines from the disengaging section to the fluorination zone or to transport of fines from the oxidation zone. (From separate laboratory tests, it was known that the vibration effectively returned powder from the disengaging section to the fluorination zone.)

Run 62 was, therefore, carried out under operating conditions similar to Run 61; however, the superficial fluidization velocity was lowered to 0.9 ft/sec in the oxidation zone and mechanical vibration was used for the entire run. Run 62 was purposely halted before completion. It was observed that 69% of the uranium compounds (3.1 lb) remaining in the oxidation zone had been reacted to U_3O_8 powder and that no accumulation of fines had occurred in the column disengaging section. Hence, it was concluded that column vibration was effective in returning powder to the fluorination zone but inadequate for fines transport from the oxidation zone. It was also concluded that with higher gas velocities, excessive elutriation of fines would occur.

At lower gas velocities, it appeared that powder transport from the oxidation to the fluorination zone might be improved by preferential oxidation in the upper part of the pellet bed. Longitudinal (axial) heat-transfer tests with fluidized-packed beds²¹ had indicated that a longitudinal temperature gradient could be imposed within the oxidation zone by allowing heat to be transferred from the fluidized alumina in the fluorination zone to the upper surface of the fluidized-packed bed (i.e., to the oxidation zone). Thus, with the upper portion of the fluidized-packed bed at a temperature high enough for rapid oxidation rates, the lower portion of the bed would be at lower temperatures and oxidation rates would be reduced. This effect was important because, with uniformly high temperatures, oxidation occurred

throughout the pellet bed; under these conditions U_3O_8 formed at the bottom of the bed had to be transported to the fluorination zone through tortuous paths in the voids of the pellet charge.

A typical temperature gradient ranged from about 400°C at the top to 100°C at the bottom of the pellet-containing bed. This gradient was established by maintaining the fluorination zone at a temperature of 500°C ; heat was conducted downward through the fluidized-packed bed constituting the oxidation zone, and the bottom flange of the reactor was cooled by natural convection of ambient air. Since the gradient lowered the general temperature level of the pellets, the effect of temperature on the oxidation rate was partially offset by use of 18 and 31% oxygen instead of the 3 to 12.5% used previously.

108-7607

Fig. 31. Bed Temperatures during Run 63. A two-zone oxidation-fluorination of uranium dioxide pellets with temperature gradients through the pellet bed.

(sq ft) and with processing times of 14 to 18 hr for 95% complete fluorination. In one run temporary stoppage of the fluidizing gas occurred (caused by external equipment failure) and the established temperature gradient was disrupted. The resulting drop in bed temperature is shown in Fig. 31 at the 5-hr mark. The effect of such a disruption is to interrupt fluorination until proper temperatures can be reestablished.

The internal fluidized-packed bed temperatures were monitored by five thermocouples welded in place at various elevations within a single longitudinal thermowell; these temperatures were continuously recorded during a run. Temperature profiles obtained during Run 63 are shown in Fig. 31. As the uppermost pellets were reacted, the relatively cool pellets surrounding a given thermocouple gradually disappeared and were replaced by the heated fluidized bed. This effect is evidenced in Fig. 31 by the increase in temperature at thermocouple positions 3, 4, and 5. Temperatures at the bottom of the fluidized-packed bed did not reach 400°C because of heat losses through the bottom flange of the reactor.

The use of thermal gradients gave promising results in Runs 63 and 64, with sustained production rates of about 31 to 36 lb UF_6 /(hr)

Gas pulsing was considered promising as an alternative method to promote fines transport to the fluorination zone. Preliminary tests with this technique were carried out in Lucite tubes containing fluidized-packed beds.²¹ In these tests it was observed that a pulse of gas (at 20 psig) imparted movement to pellet beds 6 and 12 in. deep at superficial fluidization velocities of 0.5 to 1.5 ft/sec. The sudden expansion of the pellet bed constituted a momentary increase in the void space and changed the path of gas flow through the voids of the stacked pellets. In addition, after several pulses, the pellets were rearranged in a packing configuration which offered minimum pressure drop to the fluidizing gas.

In Runs 65 and 66, both the gas-pulsing and the temperature-gradient techniques were used to promote fines transport to the fluorination zone. In Run 65, the pellet bed was completely oxidized and removed from the oxidation zone; however, only 46% of the charge was collected as the hexafluoride. The remaining uranium had deposited on the cone of the disengaging section in the form of U_3O_8 and intermediate uranium fluoride powders. In Run 66, plugging of the fluorine inlet by intermediate uranium fluorides was encountered after 1.5 hr of operation. These results indicated that the gas pulsing was very effective for promoting fines transport to the fluorination zone. Gas pulsing has an advantage over the temperature-gradient technique (used alone) in that the performance of the former is inherently insensitive to disruption by such factors as changes in gas-flow rate. It was also shown in Runs 65 and 66 that oxidation rates with 18 to 31% oxygen, even at reduced temperature, were too rapid, resulting in accumulation of unreacted fines.

The rate of oxidation (forming U_3O_8 powder) was decreased by the use of milder oxidation conditions in subsequent runs, and the fluorine feed was diluted with recycled process gas to prevent plugging of the fluorine inlet line. To reduce the rate of oxidation, the concentration of oxygen in the fluidizing gas was lowered to the range from 4.5 to 8%. In addition, emphasis was put on gas pulsing and no attempt was made to establish or maintain specific temperature gradients in the pellets. The recycle of gaseous effluent at 0.25 cfm to the fluorine inlet line insured that this line was kept free of solid particles regardless of fluctuations in the fluorine flow rates. These measures (in subsequent Runs 68, 69, and 70) led to more positive control of the oxidation and fluorination reactions with a consequent increase in UF_6 production and a reduction in the overall processing time from about 20 to 12.5 hr. The progress of a run made with these techniques is shown in Fig. 32, which depicts UF_6 production rates for Run 69. The UF_6 production rate from 5.5 to 9.0 hr of operation was well over 70 lb UF_6 /(hr)(sq ft). During this period of sustained high rate, no problems of temperature control were encountered in the column. Because of the fact that production rates did not significantly increase as a result of column vibration (4.0 to 5.5 hr), it was concluded that fines elutriation (through the fluorination zone) and accumulation in the column disengaging section had not occurred.

108-7610 Rev.

Fig. 32. Fluorine Feed Rates and Uranium Hexafluoride Production Rates for Run 69

trations. In this manner it was determined initially that oxygen used in a range from 18 to 31% with thermal gradients in the fluidized-packed bed yielded production rates which approached the desired rate of 50 lb $\text{UF}_6/(\text{hr})(\text{sq ft})$. However, when gas pulsing was used in conjunction with the thermal gradients, transport of U_3O_8 fines to the fluorination zone was improved and less oxygen was necessary. This effect is shown in the relationship between oxygen concentration and the processing time required for conversion of 90% of the UO_2 charge to UF_6 (see Table 22). The final conclusion was that 6 to 8% oxygen is the optimum concentration when U_3O_8 transport from the oxidation zone is aided by gas pulsing.

With the use of the two-zone system and with introduction of fluorine into an unhindered fluidized bed, positive temperature control of the fluorination was easily maintained.

3. Effect of Reactant Gas Concentration

The oxidation-fluorination experiments were not designed to investigate completely the effect of various parameters on the reactions. This approach would be difficult experimentally because of the number of physical and chemical processes which occur in the reactor and because of the transient conditions intrinsic in a batch process. Although the experimental program was directed toward optimizing production rates and fluorine utilization under controlled operating conditions, some additional information was also obtained on the effect of reactant gas concentrations on these parameters.

In the two-zone experiments, oxygen concentration through the oxidation zone was set at predetermined values for each run and was only changed if it was desirable to investigate the effect of other concen-

TABLE 22. Effect of Oxygen Concentration on Rate of UF_6 Production during Two-zone Oxidation-Fluorination

Run	Oxygen Concentration ^a (%)	Time to Collect 90% of UO_2 Charge as UF_6 (hr)
68	4.5	12.6
69	6	8.9
70	8	8.4

^aIn oxidation zone.

As was the case for oxygen, fluorine feed rates were preset and were changed to improve either the rate of uranium hexafluoride production or the fluorine utilization.

108-7609 Rev.

Fig. 33. Fluorine Feed Rates and Uranium Hexafluoride Production Rates for Run 70

Fluorine utilization was determined during the runs by calculation of the fluorine mass balance based upon rates of collection of uranium hexafluoride, fluorine feed rates, and average fluorine concentrations in the waste gas stream. Fluorine utilization (based on the formation of UF_6) and the overall fluorine utilization (based on the total consumption of fluorine in the reactor) were used to follow the reaction: an increase in the amount of intermediate fluorides would be indicated by an excess of the overall fluorine utilization over the utilization to form UF_6 . The actual program of fluorine feed rates and the response of the UF_6 production for Runs 69 and 70 are shown in Figs. 32 and 33. The utilization of fluorine to form UF_6 during several constant production periods for Run 70 is given in Table 23. As indicated in the

TABLE 23 Operating Conditions and Results for Run 70 A two-zone oxidation-fluorination of uranium dioxide pellets with gas pulsing

UO ₂ Pellet Charge	Weight	19.4 lb
	Bed Height	12 in
Alumina Charge ^a	Weight	15.6 lb
	Static Height above Pellets	20 in
	Size Limits (U S Mesh)	40 +170
Temperatures	Fluorination Zone	500°C
	Oxidation Zone (Pellets)	340 ≤ T ≤ 480°C
Pulsing Conditions	Frequency	2 pulses/min
	Pressure	20 psig
Oxygen Diluent	N ₂	
Fluorine Diluent	Process Off-gas at 0.25 cfm	
Run Duration	12.5 hr	
	(9.25 hr once through gas flow,	
	3.25 hr total off-gas recycle)	
Overall Fluorine Utilization	75%	

Process Time (hr)	Gas Flow				Average Fluorine Utilization to UF ₆ (%)	Average Production Rate [1b UF ₆ /(hr)(sq ft)]
	Oxidation Zone		Fluorination Zone			
	Rate (cfm)	O ₂ (%)	Rate (cfm)	F ₂ (%)		
0-3.5	1.04	8.0	1.44	10.2	69	37
3.5-8.5	1.04	8.0	1.51	14.4	86	68
8.5-9.25	1.04	8.0	1.42	9.4	46	23
9.25-12.5	(0.5 cfm gas recycle + 0.06 cfm F ₂ feed)				42	9

^aNorton Company, Blue Label Alundum.

figures and table, fluorine feed rates, and therefore the fluorine concentration, could be varied over a wide range of values. The fluorine feed rates were not limited by temperature control of the reaction but by the desired fluorine utilization.

4. Production Rates and Fluorine Utilization for the Batch Processing of UO_2 Pellets

The data in Figs. 32 and 33 and in Table 23 indicate that the rate of UF_6 production and fluorine utilization could be maintained at high levels during portions of a run. However, in the fluid-bed fluoride volatility process, the entire batch of pellets must be processed with satisfactory production rates and fluorine utilization. Since temperature control and freedom from caking were achieved by use of the two-zone oxidation-fluorination technique, evaluation of these runs was based upon the overall rate of UF_6 production and the overall fluorine utilization. The production rates and the efficiency of fluorine utilization were dependent upon control of U_3O_8 fines transport from the oxidation zone. The methods used to promote fines transport have been compared in Table 21, which summarizes conditions and results of fluorinations in the two-zone series of runs.

When U_3O_8 transport from the oxidation zone to the fluorination zone was aided by column vibration or thermal gradients in the pellet bed, production rates of $30 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ and fluorine utilization in the range from 50 to 60% were demonstrated. When these methods were superseded by the more effective gas-pulsing technique, milder oxidation conditions were required to avert overproduction of U_3O_8 fines. Overproduction of U_3O_8 fines was indicated by elutriation of fines from the fluorination zone, production of intermediate uranium fluorides, and plugging of the fluorine feed line. In Runs 69 and 70 the desired results and recommended operating conditions were obtained. In these runs the pellets in the oxidation zone were at a temperature intermediate between that of the fluorination zone (held at constant elevated temperature) and the bottom flange of the reactor. Gas pulsing and relatively low oxygen concentrations of 4.5 to 8.0% were used to achieve effective control of the rate of U_3O_8 fines formation and transport to the oxidation zone. Control over the reactions and fines transport was reflected by higher UF_6 production and fluorine utilization. With 6 to 8% oxygen and the above operating conditions, the fluorination proceeded at a production rate of $50 \text{ lb } \text{UF}_6/(\text{hr})(\text{sq ft})$ and a fluorine efficiency of 75%.

IV. CONCLUSIONS

The fluorination of UO_2 pellets in a fluidized-packed bed reactor system can be carried out at satisfactory rates in a well-controlled manner. The reaction proceeds by a two-step mechanism: partial fluorination of UO_2 to UO_2F_2 , followed by complete fluorination of UO_2F_2 to UF_6 . The rate-controlling step is the fluorination of UO_2F_2 to UF_6 . Reaction rates are higher by a factor of about 3 at 500°C than at 400°C .

Pellets of different manufacture showed different behavior during fluorination. Pellets fired in an inert atmosphere had a tendency to disintegrate into fines during fluorination, whereas pellets fired in a hydrogen atmosphere remained relatively intact while they decreased in size. The less reactive hydrogen-fired pellets are more representative of spent reactor fuels and were used in the majority of pilot-plant experiments.

Fused magnesium fluoride, commercial-grade calcium fluoride (fluorspar), fused reagent-grade calcium fluoride, zirconium tetrafluoride, and refractory-grade recrystallized α -alumina were used as the inert fluidized solid. Impurities in the fluorspar reacted with fluorine; the other materials were found to be relatively inert and mechanically stable in the presence of fluorine. The commercially available, recrystallized α -alumina was used exclusively in the latter portion of this program.

Because of the two-step reaction mechanism, the fluorination of a batch of pellets may proceed through an initial induction period, when virtually no UF_6 is produced, followed by a reaction period of high rates of production of UF_6 and high fluorine utilization. Oxygen enhanced the fluorination by the formation of U_3O_8 , which spalls from the pellet surface and mixes in the fluid bed as reactive fines of high specific surface area. Oxygen, rather than nitrogen, dilution of fluorine resulted in higher fluorination rates by a factor of 2 to 3. The efficiency of fluorine utilization was thereby increased in a given system by oxygen in the fluorine feed. Further increase in the fluorine utilization was realized by recycle of the process effluent gas containing oxygen and unreacted fluorine.

An exponential temperature coefficient for UF_6 formation of about 14 kcal/g-mole was determined for the fluorination of UO_2 pellets with both oxygen and nitrogen dilution of fluorine. At temperatures above 400°C , the rate was approximately three times faster with oxygen rather than nitrogen dilution of fluorine. With a constant pellet bed depth of 6 in. and a fluorine concentration of about 20%, a concentration of 5% oxygen was sufficient for rapid production of U_3O_8 fines at 500°C . Under these conditions, reagent gas of higher oxygen content (13% O_2) produced excessive fines and poor fluidization quality in the fluidized-packed bed.

When a batch of pellets was reacted with 21% O_2 in nitrogen at sequential temperatures of 300, 400, 500, and 600°C, the oxidation rate increased rapidly between 400 and 500°C. With 21% O_2 at 500°C, the rate of pellet oxidation was approximately 0.5 mg O_2 /(min)(sq cm initial pellet surface area) when a fluidized bed was used; without a fluidized bed the rate of oxidation was about 0.1 mg O_2 /(min)(sq cm). In a closed-loop recycle system initially containing 32% O_2 , the oxidation rate at 600°C, namely, 1.5 mg O_2 /(min)(sq cm), was three times faster than the rate at 500°C. The rates of U_3O_8 formation corresponded to production rates of 47 and 140 lb UF_6 /(hr)(sq ft reactor cross sectional area) at 500 and 600°C, respectively.

Dejacketing of simulated fuel elements followed by in situ fluorination of the pellets to UF_6 was briefly investigated. Removal of the Zircaloy-2 cladding at 500°C with 10% HCl in HF followed by fluorination of the bare pellets was found to be effective. A single-step procedure of fluorination alone was not completely effective for decladding because of the low volatility of ZrF_4 .

With simulated fuel segments of pellets clad in stainless steel, chemical removal of the cladding was not attempted. The cladding was mechanically broached to expose the pellets to reactant gases. With short 1-in. lengths of clad segments which were open at both ends, oxidation of the UO_2 to U_3O_8 in a lower zone of the reactor and simultaneous fluorination of the U_3O_8 to UF_6 in an upper zone were capable of removing some of the UO_2 from the cladding. Complete uranium removal from the cladding required exposure of the clad fuel segments to fluorine as a final step. Direct fluorination of the original clad segments was relatively slow. For longer fuel segments with slit or perforated stainless steel cladding, the two-zone operation resulted in rupturing of the cladding (due to oxidation of the UO_2 to U_3O_8) and complete uranium removal.

Fluorination of relatively deep beds of bare pellets was studied in order to demonstrate the fluorination with larger batches of oxide fuel. In these experiments, batch charges of 29 lb of pellets were used; these charges corresponded to a fluidized-packed bed depth of 18 in. in the 3-in.-dia fluid-bed reactor. Good fluidization quality could be maintained with production rates up to 25 lb UF_6 /(hr)(sq ft); however, fluorine utilization was less than 40%. The recycle of process effluent gas was used to increase fluorine utilization to approximately 75%; with this modification, fluidization quality was good for production rates which averaged only 17 lb UF_6 /(hr)(sq ft).

Improved production rates, fluorine utilization, and fluidization quality were obtained for 12-in.-deep pellet beds (19.4 lb per charge) by oxidation of the pellets to U_3O_8 in a lower reaction zone and by fluorination of U_3O_8 to UF_6 in an upper, unhindered fluidized-bed zone. In this two-zone

oxidation-fluorination, the less exothermic oxidation reaction was carried out in the fluidized-packed bed; the highly exothermic fluorination of U_3O_8 was carried out in the unhindered fluid bed, where high rates of heat transfer are possible. The major problem encountered was control over the production and transport of U_3O_8 fines from the fluidized-packed bed to the upper fluidized bed. Under recommended operating conditions, control of the production and transport of U_3O_8 powder was such that production rates of 50 lb UF_6 /(hr)(sq ft) and fluorine utilization of 75% were demonstrated under conditions of good fluidization quality.

The fluidized-packed bed techniques described above appear promising for use in the fluid-bed fluoride volatility process for the recovery of fissionable uranium and plutonium from spent nuclear fuels of the oxide type.

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VII. APPENDIX

A. Mathematical Analysis of a Gas Recycle Applied to the Fluorination of UO₂ Pellets

To quantitatively describe the operation of the gas recycle scheme in general and to assist in the planning and interpretation of experiments, the following mathematical analysis was developed.

In Fig. 34 are shown the process gas streams, their molar flow rates and compositions in the gas recycle system under study for the fluorination of uranium dioxide pellets. The quantities used are defined below:

- a = fluorine entering system, mol/hr
- b = nitrogen entering system, mol/hr
- c = recycle gas stream, mol/hr
- d = uranium hexafluoride collection rate, mol/hr
- x = mol fraction fluorine in waste gas
- y = mol fraction nitrogen in waste gas
- z = mol fraction oxygen in waste gas
- E = overall fluorine utilization
= [(fluorine entering system - fluorine leaving system)/fluorine entering system]
- E' = fluorine reactor efficiency
= [(fluorine entering reactor - fluorine leaving reactor)/fluorine entering reactor].

The flow quantities and compositions shown in the figure are for the general case in which the measured quantities are the gas additions (a, b, and c), the uranium hexafluoride product collection (d), and the waste gas composition (x, y, z). These conditions completely determine all gas flows, compositions and reaction efficiencies.

In addition to the three reactions given in Fig. 34, other reactions occur, namely,

The product, uranyl fluoride, tends to form fines in the system. Moderate amounts of these fines are considered desirable with respect to enhancing the reactivity and, therefore, the fluorine utilization. However, large quantities of fines (either UO₂F₂ or U₃O₈) tend to produce caking and are undesirable. The chief aim of developing a system for close control of reactant gases is to optimize conditions favoring a moderate and constant concentration level of the fines in the reactor. A satisfactory quantity of

For the nonsteady-state when the quantity of fines increases or decreases, the two equations are not identical and the fines accumulation would be calculated from the difference.

A similar condition holds for the utilization of fluorine in the reactor for which the two equations are

$$E' = \frac{1 - \left(\frac{b}{a}\right)\left(\frac{x}{y}\right)}{1 + x\left(\frac{c}{a}\right)}$$

and

$$E' = \frac{3\left(\frac{d}{a}\right)}{1 + x\left(\frac{c}{a}\right)}$$

The nonsteady-state accumulation of oxides in the reactor can be measured in terms of reactor oxygen efficiency, defined as

$$E'_0 = [(\text{oxygen entering reactor} + \text{oxygen generated} - \text{oxygen leaving reactor}) / (\text{oxygen entering reactor} + \text{oxygen generated})].$$

In quantities defined above

$$E'_0 = \frac{d - z\left(\frac{b}{y}\right)}{zc + d}.$$

The reason for using a recycle system is to improve fluorine economy through high overall fluorine utilization. The improvement possible by recycle can be shown by comparing the "once-through" fluorine reactor efficiency (E') with the overall fluorine utilization during recycle (E). By the material balance shown in Fig. 34, the steady-state relationship between these parameters is given by:

$$E^2 - E\left[\left(\frac{3}{2}\frac{c}{a} + 1\right)E' + \left(\frac{3}{2}\right)\left(\frac{b}{a} + 1\right)\right] + \frac{3}{2}E'\left(\frac{c}{a} + \frac{b}{a} + 1\right) = 0.$$

By the usual method of solving a quadratic equation, E may be found explicitly:

$$E = \left(\frac{3}{2}\frac{c}{a} + 1\right)\frac{E'}{2} + \left(\frac{3}{4}\right)\left(\frac{b}{a} + 1\right) \pm 1/2 \sqrt{(E')^2\left(\frac{3}{2}\frac{c}{a} + 1\right)^2 + 3E'\left[\frac{b}{a}\left(\frac{3}{2}\frac{c}{a} - 1\right) - \left(\frac{c}{2a} + 1\right)\right] + \frac{9}{4}\left(\frac{b}{a} + 1\right)^2}.$$

An illustration of the relation of E to E' for typical cases is shown in Table 24. These values show that higher recycle ratios, (c/a) , and lower nitrogen dilution factors, (b/a) , favor improved fluorine economy.

TABLE 24. Calculated Gain in Fluorine Efficiency for Typical Cases of Gas Recycle Operation

Gas Recycle Ratio $\left(\frac{c}{a}\right)$	Nitrogen Dilution Factor $\left(\frac{b}{a}\right)$	Fluorine Reactor Efficiency (E')	Overall Fluorine Utilization (E)	Gain ^a in Fluorine Utilization (%)
2	1	0.50	0.697	20
2	2	0.50	0.575	7.5
4	2	0.50	0.72	22
4	4	0.50	0.70	20
8	4	0.50	0.74	24
8	6	0.50	0.69	19
8	2	0.33	0.68	35
8	2	0.50	0.81	31
8	2	0.67	0.90	23
0 (no recycle)	$\frac{b}{a} \geq 0$	0.50	0.50	0

^aOverall fluorine utilization - fluorine reactor efficiency.