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Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part XVI. The Fluorination of UO₂-PuO₂-Fission-product Oxide Pellets with Fluorine in a 2-inch-diameter Fluid-bed Reactor

by

L. J. Anastasia, P. G. Alfredson,
M. J. Steindler, G. W. Redding,
J. G. Riha, and M. Haas

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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December 1967

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ABSTRACT

Fluorination of uranium and plutonium oxides to the volatile hexafluorides (UF₆ and PuF₆) in a fluid-bed reactor is a major step in the Argonne National Laboratory Reference Flowsheet¹ for the reprocessing of spent Zircaloy-clad UO₂-PuO₂ power-reactor fuel by fluoride-volatility methods. This fluorination step has been studied in a 2-in.-diam fluid-bed reactor using a fluid bed of refractory alumina and simulated spent-fuel pellets containing UO₂, PuO₂, and nonradioactive fission-product (F.P.) oxides. The objectives of this study were to determine the fluorination conditions required to minimize the retention of uranium and plutonium in the alumina bed, which is discarded as waste from the process.

Two general methods of reacting the pellets were used. In the two-zone method, the pellets were oxidized to fine particles of U₃O₈-PuO₂ in the bottom of the reactor. Simultaneously, the fines were transported by fluidizing action to the upper part of the reactor and there fluorinated to the volatile hexafluorides. The alternative procedure was to pulverize the pellets to fines by oxidation and then to complete the fluorination in a separate step. The latter method permitted fluorination of the pulverized pellets at temperatures below that required for rapid oxidation. A pellet-to-alumina charge ratio of 0.6, consisting of 1100 g of alumina and 650 g of pellets (containing 560 g uranium and 2.8 g plutonium), was generally used in an experiment. The two-zone step was usually carried out at 450°C for 3 hr using 20 v/o oxygen and 10 v/o fluorine; in the separate oxidation and fluorination steps, the pellets were initially oxidized for 4 hr at 450°C with 20 v/o oxygen and then fluorinated for 2 hr at 350°C with 5-16 v/o fluorine. With either method, approximately 80-100% of the uranium and about 20-75% of the plutonium in the pellet charge were reacted after completion of the initial fluorination step.

More than 99.5% of the uranium charge from the alumina bed could be routinely removed; therefore, the major effort in the study was devoted to the removal of plutonium from the alumina bed. The fluorination of plutonium required high concentrations of fluorine; therefore, the reactor off-gas was recycled to conserve the fluorine reagent. The uranium and plutonium content of the fluidized alumina bed was determined from samples taken from the bed during the recycle-fluorination periods. The recycle-fluorination step of the processing cycle used 90 v/o fluorine at 350-550°C for predetermined periods of time. The highest rates of plutonium fluorination occurred during the first few hours of recycle-fluorination at a given temperature.

Plutonium material balances of 97% were demonstrated when separate collection of most of the UF_6 product in cold traps and most of the PuF_6 product in NaF chemical traps was used. The total plutonium holdup in the reactor, about 5% of the charge, was represented by plutonium contained in fines adhering to the interior walls and filters.

A thermal-conductivity cell was used to obtain information on fluorine utilization and the rate of reaction for the major species, uranium. Average fluorine utilization ranged from 39 to 45%; reaction rates for UF_6 averaged 22-40 lb/(hr sq ft of reactor cross-sectional area). The reaction rates were fitted to a diminishing-sphere reaction model and compared with thermobalance data. At 300°C, the rate constant, k' , was $0.76 \times 10^{-3} \text{ min}^{-1}$, and at 350°C, the rate constant was $6.5 \times 10^{-3} \text{ min}^{-1}$, giving an apparent activation energy of 31 kcal/mole; these results were of the same order as results obtained in the thermobalance studies.

The limited data, which were inadequate for a complete statistical analysis, were analyzed statistically, using multiple-regression and least-squares techniques. The calculated correlation coefficients indicated that the residual plutonium in the alumina bed had a significant correlation with the UF_6 and PuF_6 production rates during the two-zone step.

When the pellets were processed by the two-zone method of oxidation and fluorination, residual levels in the alumina bed of 0.003-0.010 w/o uranium and 0.006-0.010 w/o plutonium were routinely accomplished, using a recycle-fluorination sequence totalling 12-20 hr. These residual levels corresponded to less than 0.1% of the uranium and 2.4-3.9% of the plutonium charged to the reactor. However, when cesium fluoride was added to the alumina bed at the start of a run to make the fission-product distribution more representative of radioactive fuel, residual plutonium in the alumina bed increased. With cesium added, the best recycle-fluorination sequence following the two-zone method of processing the pellets appeared to be 1 hr at 450°C, 3 hr at 500°C, and 4-5 hr at 550°C. With this sequence, pellet-to-alumina charge ratios of 0.3-1.2 were processed leaving 4.7-7.5% of the plutonium charge in the alumina bed.

Separation of the oxidation and fluorination steps appeared to be more promising for eventual process use when cesium was included in the fission products. The separation allowed greater flexibility in the choice of operating conditions when fluorinating the major species, uranium. Fluorinating uranium at 350°C and starting the recycle-fluorination at 350°C, rather than at 450°C as in the two-zone step, appeared to overcome the effects of the added cesium on residual plutonium in the alumina bed. The recommended recycle-fluorination sequence of 3 hr at 350°C, 6 hr at 350-550°C, and 1 hr at 550°C was effective in reducing plutonium in the alumina bed to 0.009 w/o plutonium, which corresponded to 3% of the plutonium charged for pellet-to-alumina charge ratios of 0.6. This recycle-fluorination sequence was used to process three batches of fuel pellets using only a single batch of alumina. An additional 3 hr of recycle-fluorination at 550°C was used in the recycle sequence for the third batch of pellets, giving a total recycle-fluorination time of 33 hr. The final alumina bed contained 0.009 w/o uranium and 0.009 w/o plutonium, which corresponded to less than 0.01% of the total uranium and 1% of the total plutonium charged to the reactor in the several batches of fuel pellets. The alumina bed was not significantly altered physically or chemically during these alumina reuse experiments, and a single alumina bed can probably be used to process several batches of irradiated fuel pellets, thus reducing the total plutonium losses in the waste alumina from the fluid-bed fluoride-volatility process.

I. INTRODUCTION

Fluid-bed volatility processes are being developed at Argonne National Laboratory for the recovery of uranium and plutonium from spent, low-enrichment, uranium dioxide, power-reactor fuels. The objective of this developmental program is to obtain the technical data required for the design of an all-volatility, commercial reprocessing plant for power-reactor fuels. Fluoride-volatility processes have significant economic advantages over current aqueous reprocessing techniques because they (1) involve fewer and simpler operations with considerable flexibility in processing conditions, (2) result in radioactive waste which is mostly in solid form, (3) can handle short-cooled fuel or fuel with a very high burnup without radiation damage to the reactants, (4) produce UF_6 (and PuF_6) which is suitable as feed for isotope separation and/or reconversion as fuel, and (5) have less stringent criticality requirements than aqueous processes.

Processes are being developed for low-enrichment UO_2 - PuO_2 fuel clad with either Zircaloy or stainless steel. However, major attention is being given to Zircaloy-clad fuel since this fuel is most likely to be used in future water-cooled power reactors. The ANL Reference Flowsheet¹ for reprocessing Zircaloy-clad UO_2 - PuO_2 fuel involves the following steps: (1) removal of the Zircaloy cladding by reaction with gaseous hydrogen

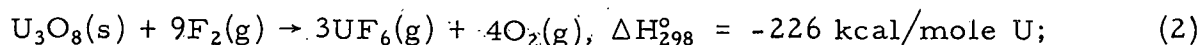
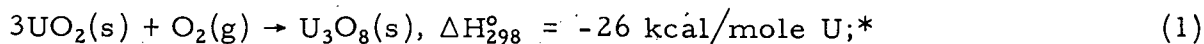
chloride to form volatile zirconium tetrachloride, which is converted to solid oxide waste by pyrohydrolysis in a second vessel; (2) fluorination of the uranium and plutonium oxides to the volatile hexafluorides, UF_6 and PuF_6 ; (3) separation of the PuF_6 from UF_6 by thermal decomposition of PuF_6 to solid plutonium tetrafluoride (PuF_4); and (4) decontamination of the UF_6 by fractional distillation, aided by solid adsorption and desorption techniques. The decladding and fluorination reactions are carried out with the fuel material immersed in a fluidized bed of inert alumina particles; the fluidized bed serves as a transfer medium for the heat liberated in the highly exothermic reactions.

In previous pilot-plant studies² with UO_2 pellets, a two-zone method of simultaneously oxidizing and fluorinating a batch of fuel pellets was demonstrated under controlled temperature conditions, high UF_6 production rates, and high fluorine efficiency. In this process, the pellets are reacted with oxygen in a lower zone containing the fluidized-packed bed of pellets, and fluorination of the resulting U_3O_8 fines with fluorine occurs in the upper fluid-bed zone of the reactor. The simultaneous oxidation-fluorination process has the disadvantage that the fluorination temperature cannot be significantly lower than the temperature required for oxidation of the fuel pellets ($\sim 450^\circ C$). Stepwise oxidation and fluorination processes have also been developed²⁻⁵ which permit greater flexibility in operating conditions, enable lower fluorination temperatures to be utilized,⁵ and allow the pulverized fuel material to be sampled to determine the uranium/plutonium ratio for accountability purposes. Subsequent fluorination with an enriched fluorine atmosphere is required for the recovery of plutonium and residual amounts of uranium from plutonium-containing fuel with both processing schemes. Fluorination of plutonium from mixtures of powdered U_3O_8 - PuO_2 -nonradioactive fission-product oxides and alumina has been investigated in boat-reactor experiments⁶ and in a laboratory-scale fluid-bed reactor.⁷ These studies showed that more than 99% of the uranium could be removed from the alumina bed using less than 20 v/o fluorine at reaction temperatures of 450 - $500^\circ C$. A fluorination sequence of 5 hr at $450^\circ C$, 5 hr at $500^\circ C$, and 10 hr at $550^\circ C$, using almost pure fluorine, was effective for the removal of 96-98% of the plutonium from the alumina. The recovery of plutonium could be further increased to greater than 99% by reuse of the alumina bed for the processing of several batches of the U_3O_8 - PuO_2 -F.P. mixture.

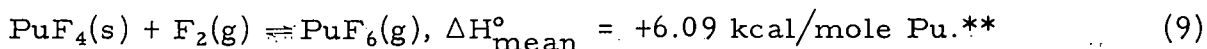
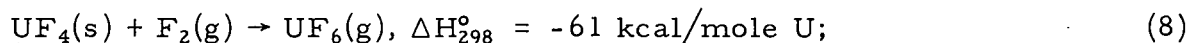
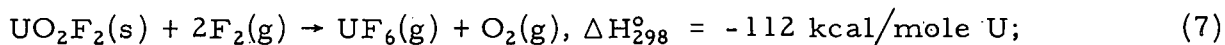
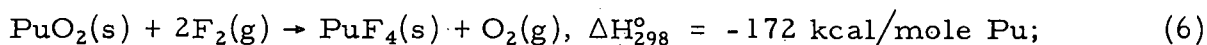
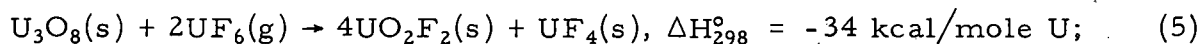
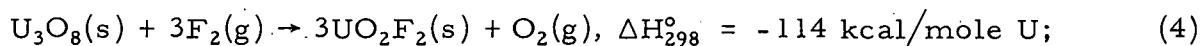
The aim of the present investigation carried out in a 2-in.-diam fluid-bed reactor was to define conditions for fluorinating UO_2 - PuO_2 -F.P. pellets which result in a minimum retention of uranium and plutonium in the fluidized bed of alumina particles. Reaction of the pellets by two-zone oxidation-fluorination was demonstrated, and subsequently, stepwise oxidation and fluorination were used to improve the removal of plutonium from alumina beds containing cesium. Major emphasis was placed on the investigation of recycle-fluorination conditions required for effective plutonium removal.

II. PROCESS CHEMISTRY

UO₂-PuO₂-F.P. pellets are processed by oxidative pulverization to U₃O₈ and PuO₂ fines, which are then fluorinated to the volatile hexafluorides (UF₆ and PuF₆). The following equations describe these reactions and give their corresponding heats of reaction:^{8,11}



Intermediate uranium fluorides and plutonium tetrafluoride may be formed during the fluorination process and subsequently reacted to the hexafluorides. For example,



Equilibrium in the system described by Eq. 9 has been investigated in the temperature range 150-400°C by Trevorrow *et al.*¹¹ The equilibrium constant $K = (\text{PuF}_6)/(\text{F}_2)$ can be expressed by the relation

$$\log K = -\frac{1331}{T(^{\circ}\text{K})} - 0.275. \quad (10)$$

*Calculated from thermodynamic data for UO₂(s) and U₃O₈(s), neglecting the effects of solid solution with PuO₂.

**Mean heat of reaction given by Trevorrow *et al.*¹¹ for 150-400°C.

III. EXPERIMENTAL DETAILS

A. Materials

The UO_2 - PuO_2 -F.P. pellets used in this investigation contained, nominally, 0.4 w/o plutonium (as PuO_2), 86 w/o uranium (as UO_2), and 1 w/o fission products (as the oxides), simulating typical, commercial, power-reactor fuels after discharge from the reactor. The pellets, 0.5-in.-diam by 0.5-in. right cylinders, contained 19 nonradioactive fission-product oxides: Ag_2O , BaO , CdO , Ce_2O_3 , Eu_2O_3 , Gd_2O_3 , In_2O_3 , La_2O_3 , MoO_3 , Nb_2O_5 , Nd_2O_3 , PdO , Pr_6O_{11} , RhO_2 , RuO_2 , Sm_2O_3 , SrO , Y_2O_3 , and ZrO_2 . Two types of pellets, subsequently referred to as Types I and II pellets, were used. Type I pellets were made from solid-solution UO_2 - PuO_2 powder mixed with fission-product oxides and sintered for 2 hr at 1600°C in nitrogen-6 v/o hydrogen to 92-94% theoretical density.¹² Type II pellets were made from UO_2 and PuO_2 powders, mixed with fission-product oxides and sintered for 6-8 hr at 1700°C in nitrogen-6 v/o hydrogen to 86-88% theoretical density. Table I shows the chemical composition of the pellets. Fission-product oxides in Type II pellets are about one-half the total weight of fission-product oxides in Type I pellets.

TABLE I. Composition of UO_2 - PuO_2 -F.P. Pellets

Oxide	Type I Pellets, ^{a,b} w/o	Type II Pellets, ^{a,c} w/o
PuO_2	0.49	0.48
UO_2	98	98
BaO	0.063	0.010
Ce_2O_3	0.11	0.079
Eu_2O_3	0.0019	0.0006
Gd_2O_3	0.0005	<0.0004
La_2O_3	0.041	0.027
Nd_2O_3	0.21	0.19
Pr_6O_{11}	0.039	0.058
Sm_2O_3	0.043	0.033
Y_2O_3	0.022	0.015
ZrO_2	0.18	0.18
MoO_3	0.24	0.094
Ag_2O	0.0005	<0.0005
CdO	0.0002	<0.002
In_2O_3	0.0002	0.0005
Nb_2O_5	0.0001	<0.0004
PdO	0.014	-
RhO_2	0.023	0.026
RuO_2	0.21	0.063
SrO	0.045	0.033

^aRepresentative of spent Dresden-type fuel after 10,000-MWd/ton burnup, 4 yr in reactor, 30-day cooled.

^bPlutonium and uranium analyses, Argonne National Laboratory; other analyses, Numec Co.

^cAll analyses, Argonne National Laboratory.

^dThis group of fission-product oxides was used in previous work on the fluid-bed fluorination of U_3O_8 - PuO_2 -F.P. oxide mixtures in a 1.5-in.-diam reactor.⁷

Preliminary experiments using UO_2 pellets were performed to evaluate the mechanical performance and reliability of the equipment. The UO_2 pellets were hydrogen-fired, nuclear-reactor-grade pellets of 94% theoretical density.

Sintered alumina, T-61* tabular alumina, nominal 48 to 100 mesh with the -170 mesh fraction removed was used as fluid-bed material in most runs. In one run, fused, high-purity α -alumina, Type RR Alundum** was used. A blend of this material (-40 +170 mesh) was prepared by screening and mixing the commercial 60, 90, and 120 mesh products. Table II gives size distributions for the sintered and fused aluminas. The spectrochemical analyses, shown in Table III, indicated that the sodium impurity was considerably higher in the Alundum material than in the T-61 alumina.

TABLE II. Particle Size Distributions of Alumina-bed Materials

Mesh	T-61 Alcoa Tabular Alumina 48 to 100 mesh Nominal, ^a w/o	Norton RR Alundum -40 +170 mesh, ^b w/o
+45	0.1	-
-45 +60	5.4	24.7
-60 +80	48.6	6.3
-80 +120	39.5	38.3
-120 +170	6.4	30.7

^aThe -170 mesh fraction was removed from the nominal 48 to 100 mesh material.

^bThe mixture was obtained by screening and mixing commercial 60, 90, and 120 mesh products.

TABLE III. Spectrochemical Analyses of Alumina-bed Materials

Element	Alcoa T-61 Tabular Alumina 48 to 100 mesh Nominal, w/o	Norton RR Alundum -40 + 170 mesh, w/o
Ca	0.01	0.01
Fe	0.09	0.06
Mg	<0.01	<0.01
Na	<0.01	0.3
Si	0.01	0.06

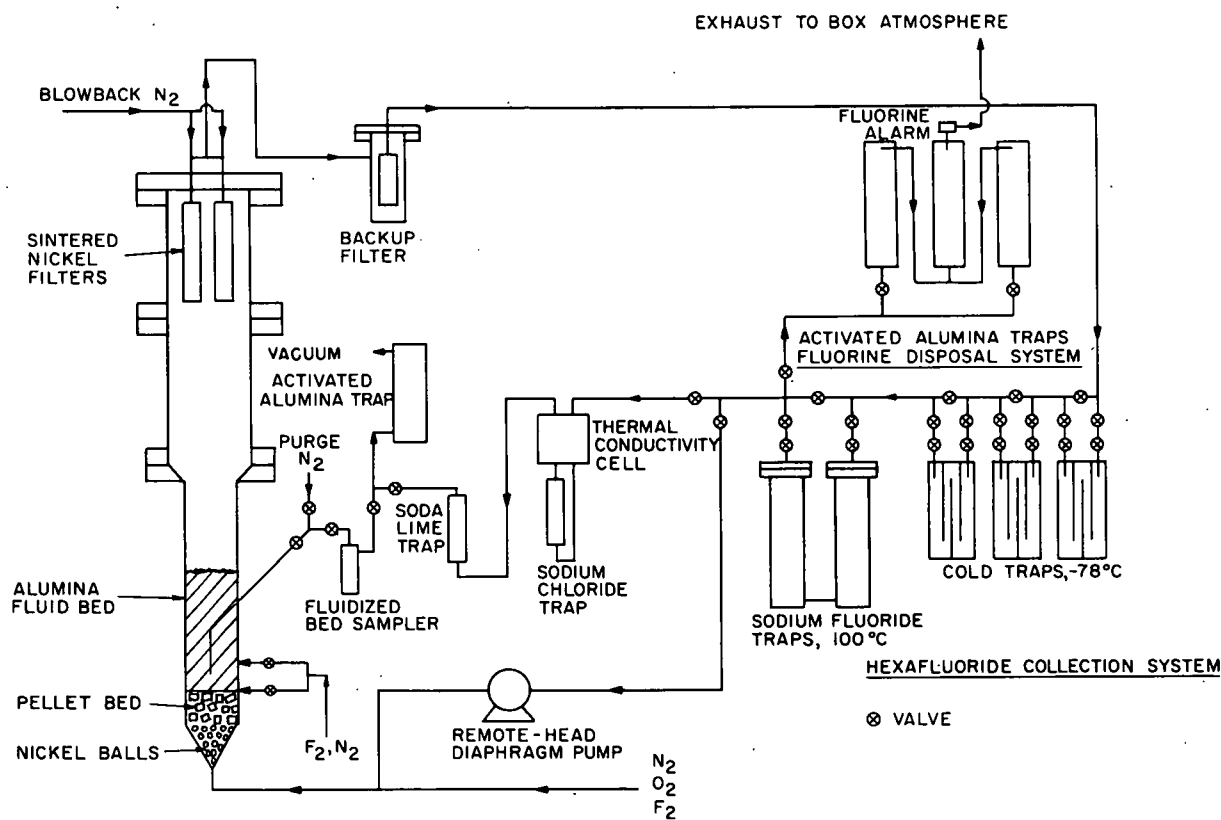
* Manufactured by Aluminum Company of America, Bauxite, Arkansas.

** Manufactured by Norton Company, Worcester, Massachusetts.

Fluorine, oxygen, and nitrogen were obtained from commercially available vendors' cylinders. Before use, the fluorine was passed through a sodium fluoride trap at 100°C to remove hydrogen fluoride, and the oxygen and nitrogen were passed through a trap containing molecular sieves to remove water vapor. Alcoa activated alumina,* 8-14 mesh, was used in chemical traps for the disposal of unreacted fluorine. The sodium fluoride pellets,** used to collect hexafluoride products were formed from sodium bifluoride and were activated by driving off HF. The activated pellets were 1/8 in. in diameter and 1/8 in. high and contained a minimum of 98% NaF. The cesium fluoride† powder added to the alumina bed was 99.9% pure with 100% <80 mesh, 40% <100 mesh, and 11% <325 mesh.

B. Equipment

The major components in the experimental system were the 2-in.-diam fluid-bed reactor, hexafluoride collection traps, a thermal-conductivity cell for fluorine analysis, chemical traps for fluorine disposal, and a remote-head diaphragm pump. These components were contained in an alpha glove-box, 10 ft wide, 3.3 ft deep, and 6.7 ft high, and are shown schematically in Fig. 1. Figure 2 is a photograph of the 2-in.-diam fluid-bed reactor. Equipment specifications are set out in Table IV.



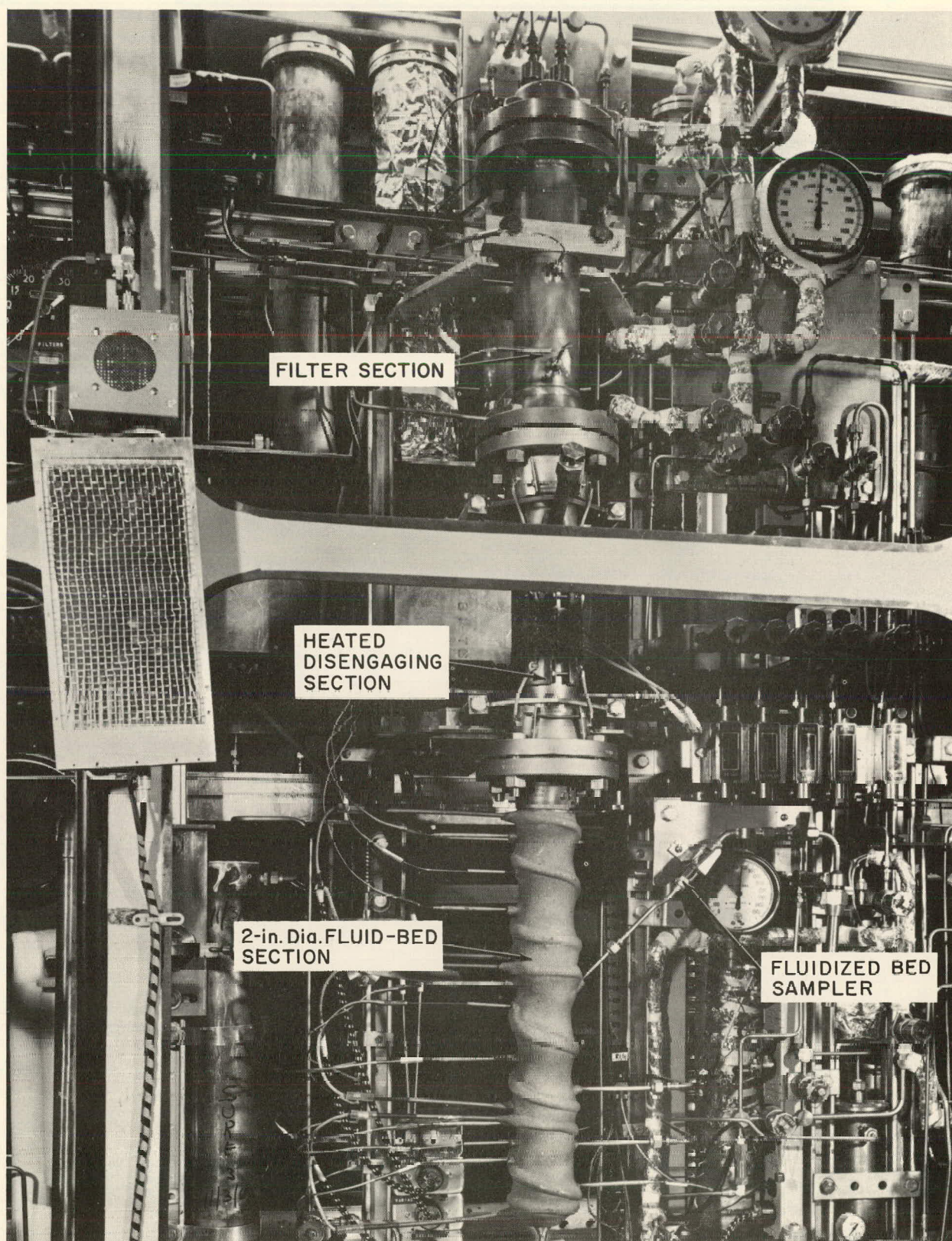
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Fig. 1. Schematic Diagram of Two-inch-diameter Fluid-bed Reactor System

* Manufactured by Aluminum Company of America, Bauxite, Arkansas.

** Manufactured by Harshaw Chemical Co., Cleveland, Ohio.

† Manufactured by City Chemical Co., New York.



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Fig. 2. Two-inch-diameter Fluid-bed Reactor

TABLE IV. Equipment Specifications for Two-inch-diameter Fluid-bed Reactor

Item	No. Used	Size or Rating	Material of Construction	Special Features
<u>Reactor</u>	1	Schedule 40 pipe	Nickel	
Fluid-bed section	1	2-in. diam x 27.5 in.	Nickel	Bed support: nickel balls (~1/4 in.). Heating capacity: 3 kW.
Disengaging section	1	3-in. diam x 17 in.	Nickel	Heating capacity: 1 kW.
Filter section	1	3-in. diam x 15.7 in.	Nickel	Two sintered nickel filters, 1-3/4 in. x 12 in. long, nominal 10- μ porosity; automatic blowback with nitrogen.
Fluid-bed sampler	1	0.25-in.-OD tube	Nickel	Two ball valves, Type 303 stainless steel, Teflon seats and packing.
Secondary filter chamber	1	2-in. OD x 8 in.	Nickel	One sintered nickel filter, 1-3/4 in. x 6 in. long, nominal 10- μ porosity. Heating capacity: 0.5 kW.
Pressure-drop recorders	2	0-15 psig	-	Pneumatic Δp transmitter with pneumatic-to-electrical transducer.
<u>Fluorine Recycle Pump</u>	1	0.5 scfm at 15 psig	Nickel	Remote-head diaphragm pump.
<u>Hexafluoride Collection System</u>				
Cold traps	3	4-in. OD x 12 in.	Nickel	Three internal baffles per trap.
Sodium fluoride traps	2	3-in. OD x 23.5 in.	Nickel	~2.5 kg of NaF per trap. Heating capacity: 0.2 kW.
<u>Thermal-conductivity System</u>				
Cell	1		Nickel	Temperature-regulated, diffusion-type, four-filament cell.
Power supply	1	0-20 V dc	-	Zero, sensitivity, and filament-current controls.
Sodium chloride trap	1	1.25-in. OD x 11.7 in.	Nickel	~0.2 kg of sodium chloride.
Soda lime trap	1	2-in. OD x 11.3 in.	Brass	~0.3 kg of soda lime.
<u>Fluorine System</u>				
Supply manifold	1	2 x 6-lb cylinder capacity	Nickel	Ballast tank; pressure regulator; exterior ventilated enclosure (see Fig. 3).
Disposal traps	3	4-in. OD x 24 in.	Copper	~3 kg of activated alumina per trap.
<u>Vacuum System</u>				
Pump	1	58 liters/min at 0.1- μ pressure	-	Exhausts to glovebox.
Activated-alumina trap	1	4-in. OD x 24 in.	Copper	~3 kg of activated alumina.
Liquid-nitrogen U-trap	1	1-in.-OD tubing x 12 in.	Copper	Pressure control and thermistor control on nitrogen level.
<u>Tubing</u>				
Oxygen, nitrogen, air		0.25- to 0.5-in. OD	Copper	
Fluorine		0.375-in.	Nickel	

The fluid-bed reactor was fabricated from three sections of Schedule 40, nickel-200 pipe: a 2-in.-diam by 27.5-in. fluidized-bed section, a 3-in.-diam by 17-in. disengaging section, and a 3-in.-diam by 15.7-in. filter section. The fluidized bed and disengaging sections were equipped with individually controlled electric heaters and associated

thermocouples to provide adequate temperature measurement and control. The main flow of fluidizing gas entered at the bottom of the reactor; fluorine could be fed through the bottom or alternatively through side inlets located 3 and 6 in. above the conical gas distributor. The distributor was filled with 0.25-in.-diam nickel balls, which supported the charge of fuel pellets. The fluid bed could be pulsed by using a nitrogen supply which was independent of the fluidizing gas; the frequency and duration of pulsing were controlled by electric timers and a solenoid valve. The fluidized bed was sampled through a 0.25-in.-OD nickel tube at a point on the axis of the reactor and 7 in. above the nickel balls.

The disengaging section of the reactor was equipped with a 0.75-in.-OD charging port, which could be used for pellet or alumina additions without dismantling the reactor. The filter section contained two bayonet-type, sintered nickel filters, 10- μ pore size and 1.75 in. wide by 12 in. long, to remove solids entrained in the reactor effluent gas. Solids collected on the filters were periodically returned to the fluidized bed by reverse flow of nitrogen. The frequency and duration of filter blowback was controlled by electric timers and a solenoid valve. A secondary, nonblowback, sintered nickel filter, 1 $\frac{3}{4}$ in. by 6 in. long, was connected in series with the process filters.

Pressure drops across the filters and the fluidized bed were measured by differential-pressure transmitters. These measurements were given by pressure indicators inside the glovebox and were also recorded outside the glovebox. The pneumatic signal from the transmitters was converted to an electrical signal by a potentiometer-type pressure transducer.

The hexafluoride collection system consisted of three baffled cold traps and two sodium fluoride traps in series. The cold traps were held at -78°C by trichlorethylene-dry ice baths; the series of cold traps had a collection efficiency of ~97% for UF₆ under normal operating conditions. The remaining hexafluoride products were removed by the sodium fluoride traps, which were maintained at 100°C. In some experiments, the first cold trap was replaced by a 2-in.-diam, 6-in.-long sodium fluoride trap, which was heated to 300-400°C to selectively remove PuF₆ from reactor off-gas. Sorption studies at ORNL¹³ showed that sodium fluoride at 350°C was highly effective in separating PuF₆ from UF₆ when sufficient excess fluorine was present to prevent the formation of a NaF-U(V) fluoride complex. Effluent gas from the hexafluoride collection system could be recirculated to the fluid-bed reactor by the remote-head diaphragm pump or passed to a series of activated alumina traps for fluorine disposal. The flow rate of the recycled gas was measured with a Mark II thermal flowmeter described by Kessie.¹⁴

The thermal-conductivity cell was used for continuous fluorine analysis of the effluent gas from the hexafluoride collection system during the initial period of fluorination when most of the uranium and plutonium

charge was present in the reactor and the fluorine concentration was less than 20 v/o. Since the effluent gas contained oxygen, nitrogen, and fluorine, whose thermal conductivities differ by only 0.05% at the pressures and temperatures of interest, the thermal-conductivity method could not be used directly. However, quantitative substitution of chlorine for fluorine by reaction with sodium chloride between the reference and sample sides of the cell (see Fig. 1) provided a component in the gas stream with a thermal conductivity one-third that of oxygen and nitrogen; consequently, continuous fluorine analysis of the off-gas was possible.¹⁵ The thermal-conductivity cell was calibrated against known mixtures of fluorine in nitrogen. The chlorine in the exit gas from the cell was removed by reaction with soda lime.

Nitrogen, oxygen, and fluorine were fed from supply cylinders located outside the glovebox and metered to the reactor system with rotameters. Glass rotameters were used for oxygen and nitrogen, and a Kel-F rotameter was used for fluorine. The fluorine supply manifold, located outside the laboratory in a ventilated mild-steel enclosure, is shown schematically in Fig. 3. Two 6-lb (400-psi) cylinders of fluorine were connected in a high-pressure manifold within aluminum cabinets located in the enclosure. The cylinder valves were operated remotely by handles extending through a concrete wall into the laboratory. Fluorine was passed from the high-pressure cylinders, through a pressure regulator for pressure reduction to a NaF trap for HF removal, and then to a low-pressure (40-psig) ballast cylinder, which supplied the reactor system.

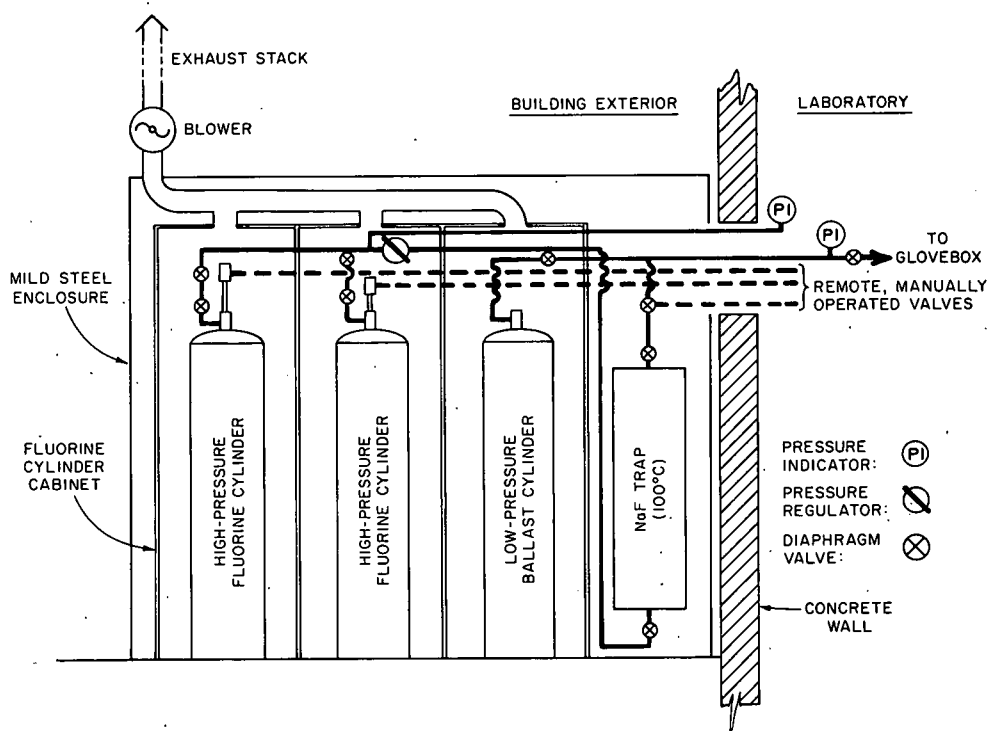


Fig. 3. Schematic Diagram of Fluorine Manifold and Supply System

C. Procedure

The 2-in.-diam fluid-bed reactor system was designed so that different operational methods for reacting the fuel pellets could be investigated. These methods include two-zone oxidation-fluorination, two-step oxidation and fluorination, single-zone fluorination using once-through gas flow, and fluorination using recycled gas. These methods and the techniques for charging the reactor and sampling the fluidized beds and NaF traps are described below. The computer program used to calculate operating conditions from basic run data is described in Appendix C.

1. Fuel Charging

Weighed quantities of fuel pellets and alumina were charged to the fluid-bed section while the reactor was disassembled. In most runs, 2-in.-deep beds of pellets (650 g) and 1100 g of alumina-bed material were used, and the bed support consisted of 200 g of 1/4-in.-diam nickel balls which filled the gas distributor cone (as shown in Fig. 1). The charge was added in the following sequence: The bed support of nickel balls was charged first, followed by about 300 g of the alumina-bed material; then the pellets were added one at a time, and finally the remainder of the alumina was charged to the reactor. This procedure eliminated the possibility of fuel pellets bridging above the sampler line in the reactor.

2. Two-zone Oxidation-Fluorination

The system was heated to the required temperatures with nitrogen passing through the reactor to maintain the alumina bed in a fluidized condition. When the fluidized-bed operating temperature of 450°C was reached, 10-20 v/o oxygen was fed to the bottom of the pellet bed to oxidize the pellets. Simultaneously, fluorine was introduced through one of the side gas inlets, 3-6 in. above the bed support of nickel balls, to fluorinate the oxide fines to the volatile hexafluorides (UF_6 and PuF_6). The fluorine flow rate was such that, when mixed with the oxygen and nitrogen fed to the bottom of the reactor, the fluorine represented ~10 v/o of the total gas flow. In a few experiments, the gas fed to the bottom of the reactor was pulsed for short periods to aid in the transport of oxide fines from the pellet-bed oxidation zone to the upper, fluidized-bed fluorination zone. Satisfactory operation was normally achieved, however, without the need for bed pulsing.

The reactor effluent gases, containing volatile hexafluorides, unreacted fluorine, oxygen, and nitrogen, were passed through the hexafluoride cold traps and backup NaF traps before passing to the activated alumina traps for disposal of fluorine. The progress of the disposal reaction in the activated alumina traps was indicated by the temperature profiles in the traps. Fluorine utilization in the fluid-bed reactor was determined by continuous fluorine analysis of the effluent gas from the hexafluoride collection system with the thermal-conductivity cell.

Approximately 80-100% of the uranium in a 650-g charge of fuel pellets was fluorinated in 3 hr of two-zone oxidation-fluorination. The extent of reaction was a function of the type and reactivity of the pellets (see Section IV.B.1). Approximately half the plutonium in the pellet charge was also reacted during this step.

3. Fluorination with Fluorine; Once-through Gas Flow

Fluorination of unreacted pellets remaining after the two-zone oxidation-fluorination step was continued by a single-zone fluorination process in which 5-10 v/o fluorine in nitrogen was fed to the bottom of the reactor. Hexafluoride product collection and fluorine disposal were similar to the two-zone step above. Fluorine in the effluent gas from the NaF traps was also measured with the thermal-conductivity cell. Less than 5% of the pellet charge remained in the fluid-bed reactor after 1 hr of reaction.

4. Two-step Oxidation and Fluorination

For experiments in which the oxidation and fluorination steps were carried out separately, the 2-in. beds of fuel pellets were oxidized with 20 v/o oxygen in nitrogen at 450°C. A reaction period of 4 hr was used to ensure complete pulverization of the pellets.

Following the oxidation step, the U_3O_8 fines resulting from the charge of 650 g of UO_2 - PuO_2 -F.P. pellets in 1100 g of alumina represented about 38.5% of the total fluidized-bed material. These fines were fluorinated by initially introducing fluorine to the fluidized bed through the upper side inlet where, it was felt, fluidizing-gas bubbles and solids movement were well developed when large quantities of fines were present. Fluorine equivalent to 5-16 v/o of the total gas flow was admitted through the side inlet until fluorine utilization was less than 50%, as determined from material balance using the input feed rate and analysis of the process off-gas with the thermal-conductivity cell. Subsequently, fluorine was fed to the bottom of the reactor to complete the fluorination. The hexafluoride products were collected in the cold traps and NaF traps, and unreacted fluorine was passed to the activated alumina traps for disposal.

More than 90% of the fines, corresponding to a 650-g charge of fuel pellets, were fluorinated at 350°C in 2 hr by this method; initially, high fluorine utilization indicated that most of the reaction took place during the first hour of fluorination.

5. Recycle-Fluorination

Residual uranium and plutonium in the alumina bed following the fluorination procedures described above were removed by further reaction with ~90 v/o fluorine at 350-550°C. During this step, consumption

of fluorine by reaction was small and the reactor effluent gases were recycled with the remote-head diaphragm pump to conserve the fluorine reagent. Continuous input of fluorine was required to maintain 90 v/o fluorine in the presence of nitrogen from filter blowback and instrument-line purges. Hexafluorides volatilized from the fluidized alumina bed were collected by sorption in the NaF traps.

6. Fines Returned to Fluid-bed Reaction Zone

In each operational method described above, it was desirable to maintain the reactive uranium-plutonium fines in the fluidized alumina bed to provide maximum reaction in each fluorination step. Fines elutriated from the fluidized bed were removed from the reactor effluent gas by the porous sintered-metal filters. To return these fines to the fluidized bed, each filter was blown back every minute during all process steps except recycle-fluorination, when the frequency of blowback was every 5 min. Nitrogen at 50 psig was used for blowback for ~0.7 sec. Further, to minimize the holdup of fines on the vertical walls of the reactor above the fluidized bed, the disengaging and filter sections were rapped with a plastic mallet, generally, every 15 min. During the initial fluorination step of a two-step oxidation and fluorination experiment, when high concentrations of uranium fines were present in the fluidized bed, the reactor was rapped every 10 min.

7. Sampling of the Alumina Bed

Samples of the fluidized alumina bed were taken through the bed sampler during the experiments to monitor the fluorination of uranium and plutonium in the reactor. In a typical sampling procedure, two bed samples were taken: the initial sample was taken as a line clean-out sample to prevent cross-contamination from previous samples and was discarded; the second sample was utilized for chemical analysis.

At the end of each run, the alumina bed from the reactor and the contents of the sodium fluoride traps were weighed and sampled for chemical analysis. The alumina bed was repeatedly passed through a sample splitter (1:1) to obtain a final sample of 10-20 g, which was ground to -300 mesh in a motorized, agate mortar and pestle. The contents of the NaF traps were pulverized in a disk-mill, and a sample of 10-20 g was obtained using a similar sample splitter.

IV. RESULTS AND DISCUSSION

A. Experiments with UO₂ Pellets

Three preliminary experiments with UO₂ pellets were performed to evaluate the mechanical performance and reliability of the equipment. These runs were similar in each respect to those with UO₂-PuO₂-F.P. pellets; i.e., a 2-in.-deep bed of pellets, 650 g, in 1100 g of Al₂O₃, was processed for several hours of two-zone oxidation and fluorination, and then the recycle-fluorination step was performed. In one run, an hour of single-zone fluorination was also used. These runs are described in detail in Table A.I in Appendix A.

Oxidation of the UO₂ pellets was demonstrated with 10-18 v/o oxygen in nitrogen for 3 hr at 450 and 500°C. Fluorine was simultaneously introduced to the reactor at 7-15 v/o of the fluidizing gas. Uranium analysis of the fluidized bed indicated fluorination of at least 99.5% of the uranium charge during the two-zone step. These results corresponded to average production rates for UF₆ of about 27 lb/(hr)(sq ft) and average fluorine utilizations of 30-70%. Since relatively constant fluorine flow rates were used with approximately the same pellet charge for each run, average production rates and fluorine utilization should be considered as parameters rather than variables for these experiments.

The average recovery of uranium as UF₆ in the product-collection system was 100.1% in these runs, and the uranium in the final alumina beds was about 0.01 w/o, corresponding to removal from the alumina bed of more than 99.9% of the uranium charge.

The experiments with UO₂ pellets demonstrated: (1) the operability and dependability of the equipment for runs totaling 13-23.5 hr; (2) simultaneous oxidation and fluorination of a batch of pellets with satisfactory production rates and fluorine utilization; and (3) satisfactory removal of uranium from the alumina bed and complete recovery of the uranium as UF₆ product.

B. Two-zone Oxidation-Fluorination of UO₂-PuO₂-F.P. Pellets

1. Reactivity of Types I and II Pellets

As discussed in Section III.A, two types of pellets were used in these studies; the pellets are referred to as separate types because of differences in the method of manufacture and in the fission-product content (see Table I). Type I pellets were used for the six initial experiments; Type II pellets were used in all subsequent experiments. Differences in chemical reactivity were noted between the Types I and II pellets when compared with UO₂ pellets. This difference was noted during the two-zone oxidation-fluorination step where the reaction could be followed by measuring the fluorine utilization through use of the thermal-conductivity cell.

With the Type I pellets a higher concentration of oxygen (20 v/o) was required at 450°C to give reaction rates approximately equivalent to those observed with UO₂ pellets and 11 v/o oxygen. Under these conditions, however, approximately 80-90% of the pellet bed was reacted during the two-zone step, corresponding to an average production rate for UF₆ of about 22 lb/(hr)(sq ft). Consequently, a single-zone fluorination procedure was used to react the remainder of the pellet bed; during this fluorination step, fluorine in nitrogen was passed to the bottom of the reactor for about an hour.

For the Type I pellets, lower reaction rates as evidenced by lower fluorine utilization were attributed to lower rates of oxidation as compared to the UO₂ pellets. Retarded oxidation rates can be attributed to the presence of fission products and plutonium dioxide.^{3,16} Type II pellets, however, reacted at rates equivalent to those obtained with UO₂ pellets. For example, after 3 hr of two-zone oxidation and fluorination of the Type II pellets at 450°C, more than 99% of the uranium and about 75% of the plutonium was fluorinated from the alumina bed. Since Type II pellets also contained fission products and plutonium dioxide, other factors (e.g., the concentration of fission products) may have also influenced the rate of oxidation.

Even though greater reaction rates were obtained with the Type II pellets than with Type I pellets, the single-zone fluorination was included in most runs to keep comparative fluorination cycles on a uniform basis. The fluorination cycles and average operating conditions for runs 1-6 with Type I pellets and runs 7-16 with Type II pellets are given in Table A.2 in Appendix A.

2. Criteria for Evaluation of Experimental Results for Fluorination of Uranium and Plutonium

Major emphasis in the experimental program was placed on the development of the recycle-fluorination sequence for removal of plutonium. Thus each experiment was evaluated primarily on the amount of uranium and plutonium remaining in the final alumina bed. Since each batch of 650 g of UO₂-PuO₂-F.P. pellets contained about 2.8 g of plutonium, a plutonium level of 0.0075 w/o in a final alumina bed of 1100 g represented 3% of the plutonium in a single batch of pellets; if three batches of pellets were processed with the same bed of alumina, then 0.0075 w/o plutonium corresponded to only 1% of the total plutonium charged. Similarly, 0.0075 w/o uranium in the alumina bed represented less than 0.1% of the uranium charged in a single batch of pellets. The effectiveness of each recycle-fluorination sequence was also evaluated by the rate of uranium and plutonium removal from the fluidized alumina bed as determined from samples taken at selected intervals during the recycle-fluorination periods. Additionally, the uranium and plutonium in the final alumina bed from each

run were obtained from a sample of the bed while still fluidized, and also from a sample obtained by riffing the alumina bed recovered from the reactor. In each of the figures depicting uranium and plutonium in the fluidized alumina bed during recycle-fluorination, data for the final bed sample are shown as two points at the terminal-process time. In most cases, the uranium and plutonium analyses of the two samples of the final alumina bed were within experimental error and in excellent agreement (e.g., see Table XII later).

3. Effect of Recycle-Fluorination Sequence on Uranium and Plutonium Fluorination

Table V compares reaction conditions and the results for experiments using Types I and II pellets. The major changes in operating variables in these runs were made in the recycle-fluorination sequence, which totaled 12-20 hr at 450-550°C. In the runs using a 20-hr recycle-fluorination sequence, uranium and plutonium in the final alumina bed amounted to 0.004 and 0.007 w/o, respectively. These results were in good agreement with previous studies⁷ in which the recycle-fluorination sequence of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C was successfully developed with U₃O₈-PuO₂-F.P. oxide powders.

TABLE V. Processing Cycles and Results for Fluorination Runs with Types I and II Pellets

		Starting Materials		Weight, g					
		UO ₂ -PuO ₂ -F.P. pellets		650					
		Uranium		560					
		Plutonium		2.8					
		Alumina		1100					
Conditions									
Step	Time, hr	Temp, °C	Superficial Velocity, ft/sec	Reactants, v/o					
				O ₂	F ₂				
1. Two-zone oxidation-fluorination	3-4	450 ^a	0.7	20-30	10				
2. Single-zone fluorination	0-2	450 ^b	0.7	-	3-10				
3. Recycle-fluorination	12-20	450-550	0.3-0.9	-	90				
Results									
Run	Recycle-Fluorination Time, hr				Pellet Type	Final Alumina Bed			
	450°C	500°C	550°C	Total		Residual Concentration, w/o		Fraction of Charge, %	
						U	Pu	U	Pu
2,3,4	5	5	10	20	I	0.004	0.007	<0.1	2.7
1	0	5	10	15	I	0.004	0.007	<0.1	2.7
5	2	3	8	13	I	0.003	0.007	<0.1	2.7
6	1	3	8	12	I	0.004	0.007	<0.1	2.7
10	1	4	8	13	II	0.010	0.010	0.02	3.9
12	1	3	8	12	II	0.006	0.006	0.01	2.4
14	1	3	8	12	II	0.004	0.008	<0.1	3.1

^aIn run 1 the two-zone step was started at 450°C and finished at 500°C.

^b500°C in run 1.

Figure 4 depicts the plutonium in the fluidized alumina bed during 20 hr of recycle-fluorination in run 4. In general, each increase in temperature during the recycle-fluorination is characterized by an initial period of high fluorination rates followed by a period in which the fluorination rate diminishes. This description is also generally true for uranium, as is shown in the graphs of Appendix B.

Since the highest rates of plutonium removal occurred during the first few hours of recycle-fluorination at a given temperature, the overall recycle-fluorination sequence could be reduced without adversely affecting the final plutonium retention on the alumina. Table V shows that recycle-fluorination sequences of 12-15 hr were as effective for removal of both uranium and plutonium as the 20-hr recycle-fluorination period. This result is also illustrated in Fig. 5, which shows uranium and plutonium in the fluidized alumina bed during a recycle-fluorination sequence consisting of 2 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. This recycle-fluorination sequence took advantage of initially high reaction rates at each temperature and reduced processing time by omitting periods when fluorination rates were expected to be low.

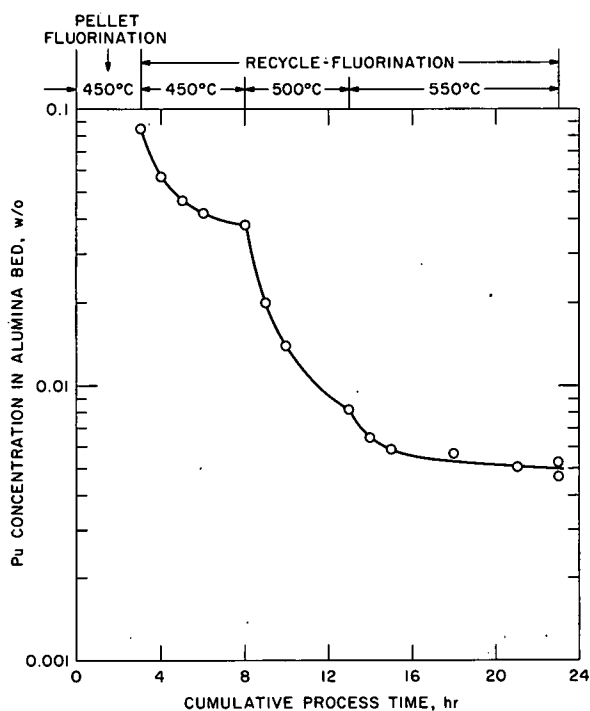
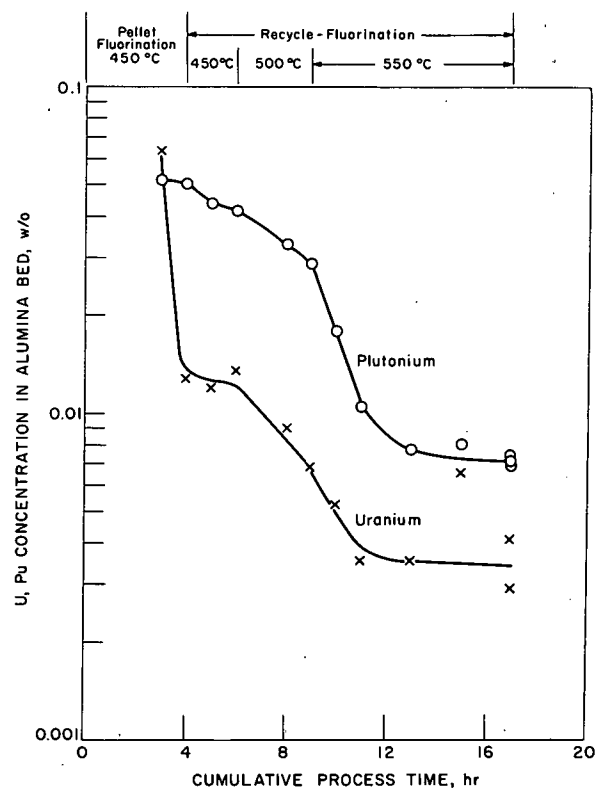


Fig. 4. Plutonium Concentration in the Fluidized Alumina Bed during Run 4



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Fig. 5. Uranium and Plutonium Concentration in the Fluidized Alumina Bed during Run 5

4. Effect of Pellet-manufacturing Method on Uranium and Plutonium Fluorination

As discussed in Section IV.B.1 above, a marked difference in reactivity between Types I and II pellets was observed during the two-zone step. Since Type II pellets were used for runs 7-22, it was of interest to

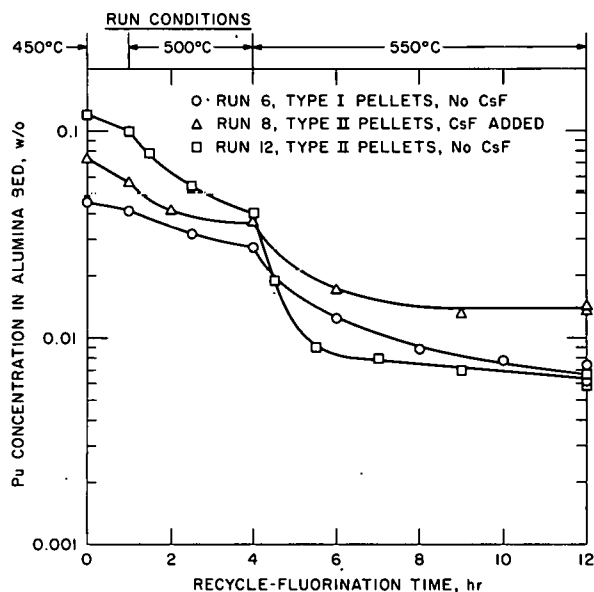


Fig. 6. Plutonium Concentration in the Fluidized Alumina Bed during the Recycle-Fluorination for Runs 6, 8, and 12

for a single use of the alumina bed. The final uranium and plutonium concentrations in the alumina bed were apparently independent of variations in operating conditions among the runs. The results from runs 5, 6, 10, 12, and 14 (listed in Table V) show that the reproducibility of the experimental data is satisfactory for this type experiment and that the final uranium and plutonium concentrations are essentially the same for Types I and II pellets despite significant differences in fabrication methods, fission-product content, density, and perhaps microstructure (e.g., solid solutions, grain size, and nature of porosity).¹⁷

C. Two-zone Oxidation-Fluorination of UO₂-PuO₂-F.P. Pellets with Cesium Fluoride Added to the Alumina Bed

Cesium, a fission product of high yield, was not included in the UO₂-PuO₂-F.P. pellets since suitable cesium compounds (i.e., oxide or fluoride) have low decomposition temperatures or boiling points and would be lost from the pellet mixture during the sintering process. Cesium fluoride may form compounds with several constituents of the fluid-bed mixture⁶ and could change the volatility of the products in the process. Therefore, to simulate more closely the fission-product distribution that

determine whether the observed difference in reactivity influenced the subsequent fluorination of uranium and plutonium during the recycle-fluorination period. Consequently, several replicate experiments (runs 10, 12, and 14) were completed with Type II pellets and compared with similar experiments (runs 5 and 6) made with Type I pellets. Table V gives the results of these runs. Figure 6 compares the fluorination of plutonium from the fluidized bed during run 6 with Type I pellets and run 12 with Type II pellets.

In each run with either Types I or II pellets, residual uranium in the alumina bed was usually less than 0.1% and residual plutonium was about 3% of the charge

might exist in the reprocessing of irradiated fuel, the alumina beds for run 7 and all subsequent runs except runs 10, 12, and 14 contained cesium fluoride.

Without cesium fluoride in the alumina bed, a shortened recycle-fluorination scheme, consisting of 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C, was effective for the reduction of plutonium in the alumina beds to satisfactory levels of about 0.007 w/o plutonium with either the Types I or II pellets (see Table V). When this same recycle-fluorination scheme was used in a run with cesium fluoride, both plutonium and uranium concentration in the final alumina bed increased. As shown in Table VI for run 8, the increase was about a factor of two for plutonium and about a factor of five for uranium. In Fig. 6, comparison of plutonium in the alumina bed during recycle-fluorination in runs 8 and 12 shows diminished reaction rates at 550°C in the presence of cesium fluoride with a consequent leveling-off of the plutonium at a higher level after 5 hr of recycle-fluorination. A similar situation is also apparent at 450 and 500°C as shown in Fig. 7 for run 4 without cesium fluoride and for run 9 with cesium fluoride, using a recycle-fluorination sequence consisting of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C. The final alumina bed for run 9 contained 0.021 w/o plutonium, which was higher than the 0.014 w/o plutonium obtained in run 8 with only 12 hr of recycle-fluorination.

TABLE VI. Processing Cycles and Results for Experiments with Alternative Recycle-Fluorination Schemes

Starting Materials ^a		Weight, g	
UO ₂ -PuO ₂ -F.P. pellets		650	
Uranium		560	
Plutonium		2.8	
Alumina		1100	
CsF		0.6	

Conditions					
Step	Time, hr	Temp, °C	Superficial Velocity, ft/sec	Reactants, v/o	
				O ₂	F ₂
1. Two-zone oxidation-fluorination	3	450	0.7-0.8	19-21	7-9
2. Single-zone fluorination	1.5-2	450	0.6-0.7	-	5-12
3. Recycle-fluorination	8.5-20	450-550	0.8-1.05	-	90

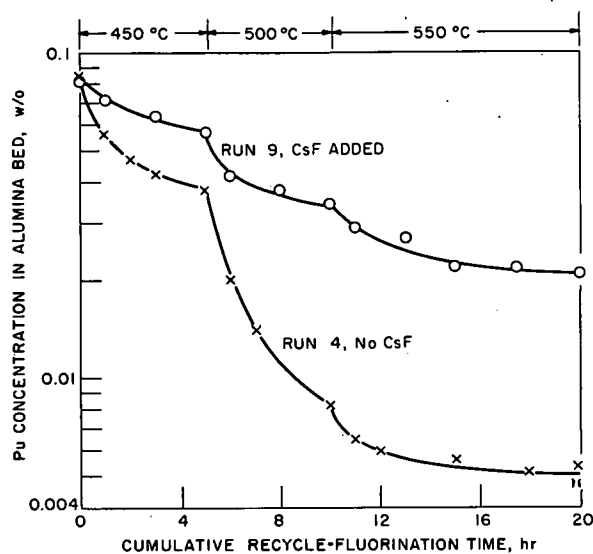
Results								
Run	Recycle-Fluorination Time, hr				Final Alumina Bed			
	450°C	500°C	550°C	Total	Residual Concentration, w/o		Fraction of Charge, %	
					U	Pu	U	Pu
9	5	5	10	20	0.021	0.021	<0.1	8.2
8	1	3	8	12	0.024	0.014	<0.1	5.5
7	1	0.5 ^b	7	8.5	0.018	0.018	<0.1	7.1
15	1	3 ^c	4	8	0.037	0.025	<0.1	9.8
16	1	6 ^d	1	8	0.015	0.034	<0.1	13.4

^aFor Run 15, 718 g of pellets, 1200 g of Al₂O₃, and 0.65 g of CsF were used.

^bReactor temperature increased from 450 to 550°C in 0.5 hr.

^cReactor temperature increased from 450 to 550°C at 5°C/9 min.

^dReactor temperature increased from 450 to 550°C at 5°C/18 min.



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Fig. 7. Plutonium Concentration in the Fluidized Alumina Bed during Recycle-Fluorination for Runs 4 and 9

uranium from the alumina bed. However, the final alumina bed from run 16 contained 0.034 w/o plutonium, but in runs 15 and 7, with a more rapid temperature increase from 450 to 550°C, the final bed contained 0.025 and 0.018 w/o plutonium, respectively. These results corresponded to residual plutonium levels of 7.1 to 13.4% of the plutonium charge.

Of the recycle-fluorination sequences described in Table VI, the one used in run 8 appeared the most promising and, as shown in Fig. 6, the recycle-fluorination sequence could be reduced to only 1 hr at 450°C, 3 hr at 500°C, and 4 or 5 hr at 550°C.

Under the conditions used in the experiments listed in Table VI, the presence of cesium in the fluid bed appeared to interfere with the fluorination of plutonium, and other conditions and procedures (described in Section IV.D) were devised to improve the removal of plutonium from the alumina bed.

2. Effect of Pellet-to-Alumina Charge Ratio

Three experiments (runs 8, 11, and 13) were performed to determine the effect of pellet-to-alumina charge ratio on plutonium volatilization from the alumina bed under identical recycle-fluorination conditions. In these runs, $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellet charges of 0.33, 0.65, and 1.32 kg were used with 1100 g of alumina corresponding to pellet-to-alumina charge ratios of 0.3, 0.6, and 1.2, respectively. The corresponding pellet-bed depths were 1, 2, and 4 in. In each run, cesium fluoride was added to the alumina bed in proportion to the pellet charge, i.e., 0.6 g of CsF for each 0.65 kg of pellets.

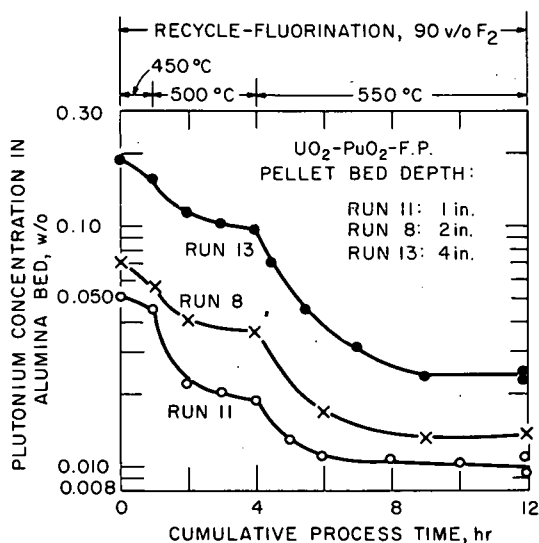
1. Evaluation of Alternative Recycle-Fluorination Procedures

Table VI shows the results of several experiments in which the recycle-fluorination was shortened to about 8 hr. The recycle sequences for these experiments featured a programmed increase in reactor temperature. In run 7, the reactor temperature was increased from 450 to 550°C in 0.5 hr; in run 15, increments of 5°C/9 min were used for 3 hr; in run 16, the increments were 5°C/18 min for 6 hr.

In each run listed in Table VI, the indicated volatilization showed a satisfactory removal of

The pellets were reacted in the following sequence: two-zone oxidation-fluorination, single-zone fluorination at 450°C, and then recycle-fluorination for 1 hr at 450°C, 3 hr at 500°C, and 8 hr at 550°C. The duration of the two-zone oxidation-fluorination and the single-zone fluorination steps was 2 hr in run 11 with the 1-in. bed of pellets, 5 hr in run 8

with the 2-in. bed of pellets, and 6 hr in run 13 with the 4-in. bed of pellets. During the two-zone and single-zone reaction periods, 99% of the uranium charge and 60-70% of the plutonium charge was volatilized from the alumina bed. Plutonium concentrations in the alumina beds during recycle-fluorination in these runs is shown in Fig. 8, and complete operating conditions are given in Appendix A.



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Fig. 8. Plutonium Concentration in the Fluidized Alumina Bed during Recycle-Fluorination for Runs 8, 11, and 13

The final alumina beds contained 0.010, 0.020, and 0.030 w/o uranium in the runs with the 1-, 2-, and 4-in. pellet beds, respectively. In each case, these results corresponded to less than 0.1% of the uranium charged. As shown in Fig. 8, the reaction of plutonium during recycle-fluorination produced similar curves, and the concentration of plu-

tonium in the final alumina bed increased as the amount of plutonium at the start of the recycle-fluorination increased. For runs with the 1-, 2-, and 4-in. beds of pellets, the final alumina bed contained 0.010, 0.014, and 0.024 w/o plutonium, respectively. These results correspond to 7.5, 5.3, and 4.7% of the plutonium charge (for pellet-to-alumina ratios of 0.3, 0.6, and 1.2, respectively). Thus, plutonium retention in the alumina bed did not increase in proportion to changes in the pellet charge. Consequently, the relative removal of plutonium from the alumina bed was improved by increasing the pellet-to-alumina charge ratio from 0.3 to 1.2. An empirical equation relating plutonium in the final bed and the initial pellet to alumina weight ratio is given by

$$\ln P = 0.96R - 4.9,$$

where

P = plutonium in final alumina bed, w/o,

and

R = pellet-to-alumina charge ratio, g/g.

If extrapolation beyond the stated pellet-to-alumina charge ratios is not extreme, this equation may be used to estimate, for identical recycle-fluorination conditions, the plutonium losses in an alumina bed for various pellet-to-alumina charge ratios.

As was stated in Section IV.C.1, when cesium fluoride was added to the alumina bed for two-zone oxidation-fluorination experiments, the best recycle-fluorination sequence for removal of plutonium was 1 hr at 450°C, 3 hr at 500°C, and 4 or 5 hr at 550°C. As is evident in Fig. 8, this statement would also be true for experiments using pellet-to-alumina charge ratios of 0.3-1.2.

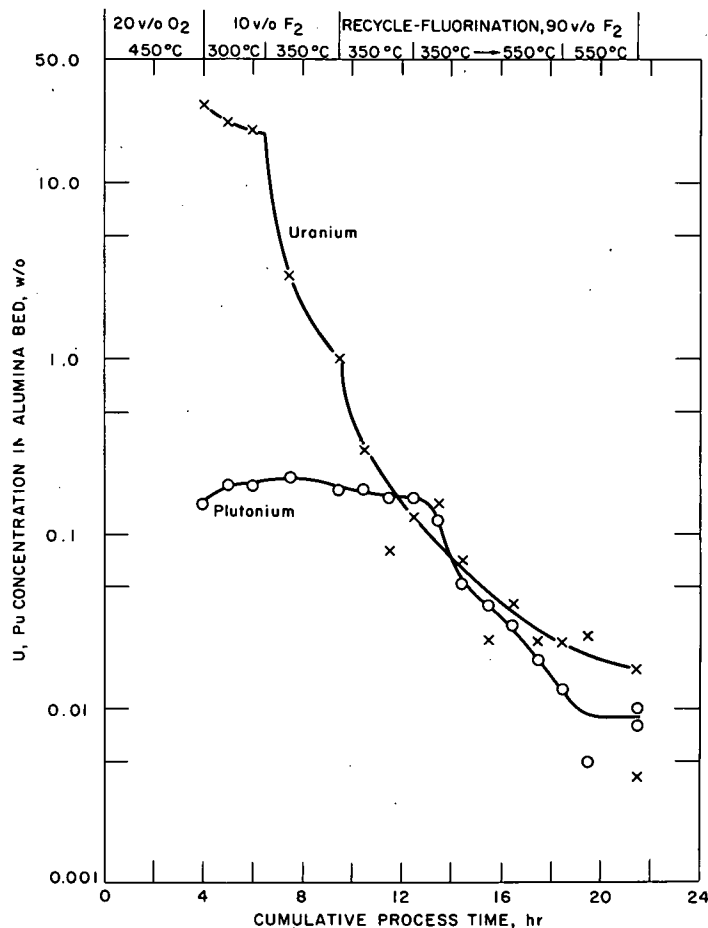
D. Oxidation and Fluorination of UO₂-PuO₂-F.P. Pellets

Separate experiments¹⁸ with an interhalogen fluoride-volatility process using BrF₅ and fluorine showed that an initial low temperature of plutonium fluorination with fluorine (about 300°C) and/or removal of approximately 99% of the uranium with BrF₅ before volatilization of plutonium may be important in achieving a low final plutonium content in the alumina bed when cesium fluoride is present. Consequently, a processing sequence using separate oxidation and fluorination steps and fluorine as the fluorinating agent was developed. The process steps were: (1) 4 hr of pellet oxidation at 450°C with 20 v/o oxygen in nitrogen, (2) low-temperature fluorination of uranium with 5 to 16 v/o fluorine, and (3) recycle-fluorination with 90 v/o fluorine at elevated temperatures for the fluorination of plutonium. Oxidation conditions were kept uniform from run to run to ensure complete pulverization of the pellets.

1. Fluorination of Uranium from Pulverized Pellets

Following the oxidation of 650 g of UO₂-PuO₂-F.P. pellets in 1100 g of Al₂O₃, the fluidized bed is expected to contain 38.5 w/o fine material resulting from pulverization of the pellets, corresponding to 31.4 w/o uranium and 0.16 w/o plutonium. After low-temperature fluorination of the uranium, the original plutonium would amount to 0.25 w/o of the total fluid-bed material.

In run 17, the initial low-temperature fluorination of uranium was attempted at 300°C with 10 v/o fluorine; under these conditions, the uranium fluorinated slowly, as shown in Fig. 9. Average production rates for UF₆ were about 20 lb/(hr)(sq ft) during the first hour of fluorination. During the second hour, the rate decreased to 9 lb/(hr)(sq ft); in the subsequent half-hour, the rate was only 1 lb/(hr)(sq ft). Thus, after 2.5 hr of fluorination, only 30-40% of the uranium charge had been fluorinated at 300°C; consequently, the temperature was increased to 350°C, where production rates for UF₆ were about 25 lb/(hr)(sq ft) during the first hour



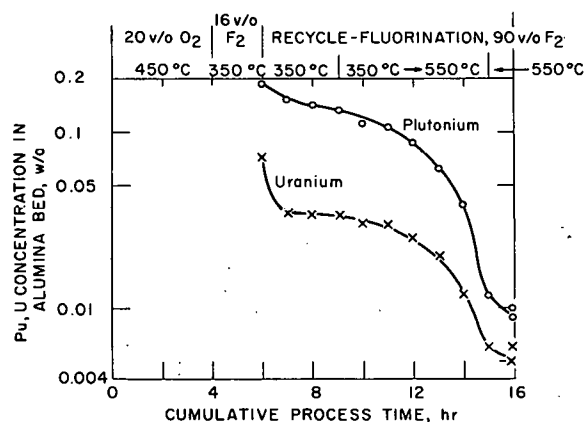
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Fig. 9. Uranium and Plutonium Concentration in the Fluidized Alumina Bed during Run 17

was carried out at 350°C in all subsequent runs. Complete operating conditions for runs utilizing separate oxidation and fluorination steps (runs 17 to 22) are given in Table A.III of Appendix A.

The analytical data in Fig. 9 and the fluorine-utilization data determined by means of the thermal-conductivity cell were fitted to a diminishing-sphere reaction-rate model to compare the U_3O_8 fluorination rates observed in the fluid bed with those obtained in thermobalance tests by Jarry *et al.*¹⁹ The model assumes that the gas-solid reaction occurs on the surface of particles with uniform diameter at a continuously diminishing spherical interface. According to this

and averaged 10 lb/(hr)(sq ft) during the two subsequent hours of fluorination. The uranium concentration in the alumina bed during a subsequent experiment (run 18, see Fig. 10) showed that a 2-hr fluorination period at 350°C with 16 v/o fluorine was sufficient to fluorinate most of the uranium-to-hexafluoride product; this result corresponded to an average production rate for UF_6 of about 40 lb/(hr)(sq ft). Continuous fluorine analysis of the reactor off-gas with the thermal-conductivity cell and fluorine-utilization calculations indicated that most of the reaction took place during the first hour of fluorination at 350°C. The production rates observed at 350°C were more representative of projected rates for the full-scale process than those obtained at 300°C; therefore, the uranium fluorination step



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Fig. 10. Uranium and Plutonium Concentration in the Fluidized Alumina Bed during Run 18

model, the integrated rate expression describing a reaction in which the surface reaction is rate-controlling is given by

$$(1 - F)^{1/3} = 1 - k't,$$

where

F = the fraction of solid reacted,

$$k' = k/r_0\rho,$$

r_0 = initial radius of reacting particles,

ρ = bulk density,

and

t = reaction time.

For run 17, the analytical data for uranium in the fluidized bed were used to determine the fraction of uranium reacted at a given temperature and to estimate, by interpolation, the initial uranium content for the 350°C fluorination period. Since much of the reaction occurred during the first hour of fluorination, at both 300 and 350°C, data from the thermal-conductivity cell were used to determine fluorine utilization and to estimate the reaction-rate constants. These calculations assumed that all fluorine consumed appeared as the most significant volatile product, UF_6 , and that the formation of solid uranium, plutonium, and fission-product fluorides was negligible. Total hexafluoride product, determined from integration of thermal-conductivity data and from the analyzed uranium content of fluidized-bed samples, agreed within 12% at 300°C and 5% at 350°C. Figure 11

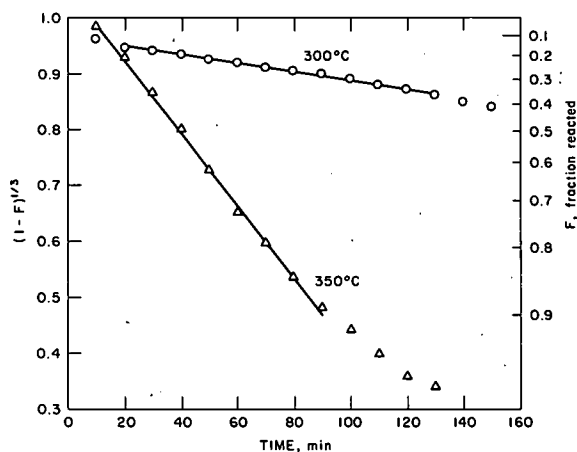


Fig. 11. Rate of Reaction of U_3O_8 with 10 v/o Fluorine in Nitrogen in a Fluid-bed Reactor

shows the extent of reaction calculated from thermal-conductivity data. Deviations from the expected kinetics at the beginning and end of the reaction periods may be due to dilution and depletion of reagents,¹⁹ formation and fluorination of intermediate fluorides, and possibly other circumstances.

A least-squares analysis of the data in Fig. 11 gives reaction-rate constants, k' , of $0.76 \times 10^{-3} \text{ min}^{-1}$ at 300°C and $6.5 \times 10^{-3} \text{ min}^{-1}$ at 350°C with an apparent activation energy of 31 kcal/mole. These results, obtained

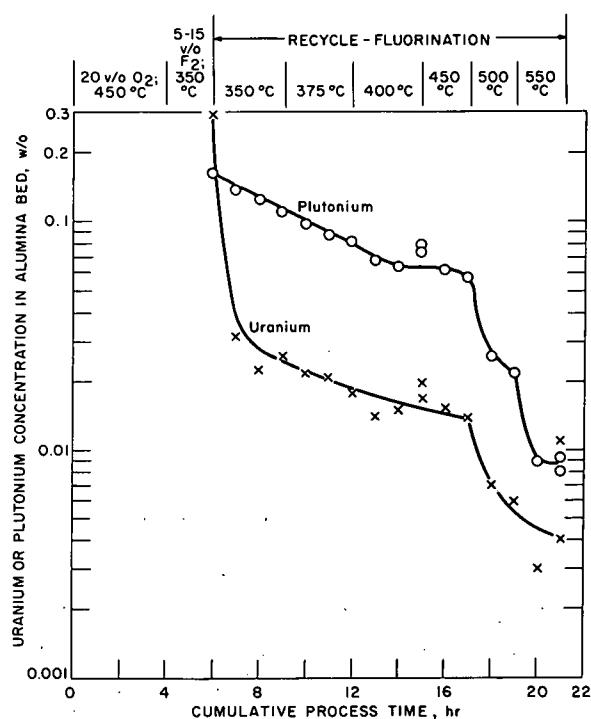
with 10 v/o fluorine in nitrogen, are of the same order as the rates obtained with the thermobalance using 100% fluorine. For two different sources

of U_3O_8 , rate constants of 0.4×10^{-3} and $0.6 \times 10^{-3} \text{ min}^{-1}$ at 300°C and 3.5×10^{-3} and $5.0 \times 10^{-3} \text{ min}^{-1}$ at 350°C were obtained in the thermobalance studies; these rates correspond to an apparent activation energy of 30 and 31 kcal/mole.¹⁹ These results suggest that thermobalance data and the diminishing-sphere reaction model can be used to predict the fluorination rates of U_3O_8 in a fluid-bed reactor.

Since the inlet pressure of fluorine to the fluidized bed was 150 mm Hg, while that in the thermobalance was 760 mm Hg, almost identical rate constants obtained at the same temperature in the two systems indicate that: (1) greater reaction rates are obtained in the fluid-bed reactor, possibly because of better gas-solids contacting; (2) more reactive U_3O_8 was encountered in the fluid bed, possibly because of smaller particle size and higher surface area; and (3) the effect of fluorine pressure on the rate of reaction, within the experimental limits for the two systems, may be negligible.

2. Fluorination of Plutonium and Residual Uranium

The plutonium content of fluidized-bed samples taken during runs 17 and 18 (plotted in Figs. 9 and 10) showed a rather sharp decrease when reactor temperature was increased from 350°C to approximately 450°C in steps of 5°C every 9 min. Consequently, one additional experiment (run 22) was completed with an extended recycle-fluorination time of



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Fig. 12. Uranium and Plutonium Concentration in the Fluidized Alumina Bed during Run 22

9 hr below 450°C to decrease the plutonium content in the final alumina bed. Plutonium content in the fluidized bed for this run is shown in Fig. 12. For the initial 8 hr of recycle-fluorination, the apparent rate of plutonium fluorination averaged 140 mg of plutonium per hour from 350 to 450°C , while at 500°C the average rate of plutonium fluorination was higher (200 mg of plutonium per hour). These rates correspond to about 0.02 lb of PuF_6 per (hr)(sq ft).

The diminishing-sphere model was applied to the fluorination of plutonium during recycle-fluorination for run 22. A fit of the data was obtained at 350 and 375°C , indicating an estimated rate constant for both temperatures of $0.55 \times 10^{-3} \text{ min}^{-1}$, which was about a factor of 6 less than those obtained when PuF_4 was

fluorinated in boat-reactor experiments.²⁰ At other temperatures in the recycle-fluorination for run 22, the diminishing-sphere model did not adequately describe the fluorination of plutonium. This was possibly due to (1) the limited number of data points that could be obtained during the run, which was not designed for a kinetic study; (2) the diminishing quantity of plutonium-bearing reactant as higher temperatures were reached; and (3) a change in the mechanisms controlling the reaction rate.

In runs 17, 18, and 22, the uranium content of about 0.01 w/o or less in the final bed of alumina corresponded to less than 0.1% of the uranium charge (see Figs. 9, 10, and 12). Similarly, the final beds in these runs contained about 0.009 w/o plutonium, indicating that approximately 3% of the plutonium charge remained with the alumina beds. Since the major portions of the recycle-fluorination sequence used in runs 17 and 18 were the same, differences in the UF₆ production rates during the uranium fluorination step apparently had little influence on the final plutonium concentration in these runs. When the recycle-fluorination step was started, less than 20% of the plutonium charge had been volatilized; therefore, the plutonium content in the alumina bed at the start of recycle-fluorination was about 0.2 w/o in both runs. However, in run 17 the alumina bed contained 1.0 w/o uranium at the start of recycle-fluorination, and in run 18, 0.074 w/o uranium. Thus, the U/Pu ratios in the alumina beds at the start of recycle-fluorination differed by a factor of 14, but this difference apparently had little influence on the plutonium content of the final alumina beds.

In comparison with all previous runs which used two-zone oxidation-fluorination at 450°C, the processing sequence used in runs 17, 18, and 22 appears more promising for eventual process use with fluorine as the fluorinating agent. With separate oxidation and fluorination steps, most of the uranium can be reacted at a lower temperature than now appears feasible for two-zone oxidation-fluorination, in which the uranium fluorination temperature is limited by slow pellet-oxidation rates below 400°C. This lower fluorination temperature and a lower initial temperature for recycle-fluorination beneficially affects the plutonium concentration in the final alumina bed when cesium fluoride is present.

E. Reuse of an Alumina Bed to Process More than One Batch of Fuel Pellets

The reuse of a single batch of alumina to process more than one batch of fuel pellets was investigated as a means of minimizing the total plutonium losses associated with the disposal of waste fluid-bed alumina. In addition to reducing total plutonium losses, a reuse of the alumina bed would result in smaller quantities of solid radioactive waste requiring disposal or long-term storage. The accumulation of fission products with

their consequent heat generation would be limited by the heat-transfer capacity of the fluid-bed reactor and maximum permissible centerline temperatures in long-term waste-storage vessels. Thus, the total quantity of fuel pellets that could be processed using a single batch of alumina would also be limited.

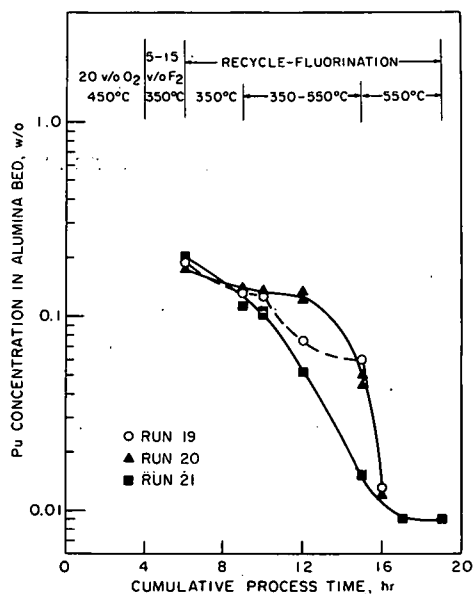
In previous studies^{6,7} of the reuse of alumina beds, a recycle-fluorination sequence of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C was required for effective plutonium removal from each batch of fuel added to the alumina bed. Before the recycle-fluorination step, an initial fluorination step was used in which most of the uranium as well as about half the plutonium was volatilized. In the present studies, the alumina-reuse experiments (runs 19, 20, and 21) were performed in a similar manner. The pellets were initially pulverized by oxidation, which was followed by fluorination of most of the uranium and some of the plutonium with 5 to 15 v/o fluorine at 350°C and then removal of most of the plutonium by recycle-fluorination with 90 v/o fluorine from 350 to 550°C. Thus, runs 19, 20, and 21 used the entire processing sequence of run 18 for each of the three batches of fuel, but used only one alumina bed. Specifically, for runs 19 and 20, the recycle-fluorination sequence consisted of 3 hr at 350°C, 6 hr at 350-550°C with reactor temperature increased 5°C/9 min, and 1 hr at 550°C, while in run 21 the reaction time at 550°C was extended from 1 to 4 hr. In each run, the weight ratio of pellets to alumina was kept constant at about 0.6 so that a uniform basis for comparing the runs is available. Cesium fluoride added to the alumina was proportioned according to the pellet charge. The alumina beds for runs 20 and 21 each consisted of the final alumina bed plus the line cleanout samples (see Section III.C.7) from the immediately preceding run. Table VII lists the materials charged to the reactor for the alumina-reuse experiments.

TABLE VII. Materials Charged to the Reactor
for Alumina-Reuse Experiments

Run	CsF, g	Alumina Bed, g		Materials Charged to Reactor, g		
		Fresh	Reused	Pellets	U	Pu
19	0.65	1200	-	720	620	3.10
20	0.61	-	1115 ^a	650	560	2.80
21	0.53	-	970 ^b	578	500	2.48
Total Charge	1.79	1200	-	1948	1680	8.38

^aIncludes line cleanout samples from previous run and contained 0.22 g of plutonium.

^bIncludes line cleanout samples from previous run and contained 0.24 g of plutonium.



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Fig. 13

Plutonium Concentration in a Fluidized Alumina Bed Used to Process Several Batches of Simulated Fuel Pellets during Runs 19, 20, and 21

The fluidized-bed samples taken at 17 and 19 hr of process time in run 21 showed that the plutonium content in the fluidized bed reached a steady value of 0.009 w/o during recycle-fluorination at 550°C. A riffled sample of the final 615-g alumina bed, removed from the reactor, had a plutonium content of 0.012 w/o. This increase was probably due to fines falling from the upper parts of the reactor into the alumina bed when fluidization was stopped. In all, 23.4 g of fines were recovered from the upper parts of the reactor by rapping and brushing. These fines contained 2.7 w/o plutonium, and an X-ray diffraction pattern showed their major phases to be U_3O_8-x and AlF_3 , and their minor phases to be $\alpha-Al_2O_3$ and possibly PuO_2 . Thus, if 0.7 g of these fines fell into the final alumina bed from run 21, the plutonium content of the bed would increase from 0.009 to 0.012 w/o.

It is believed that the fines accumulated by elutriation during the pellet pulverization steps when the fluidized bed contained about 38.5 w/o fine particles, which were mostly U_3O_8 and PuO_2 . The uranium and plutonium compounds identified by X-ray diffraction would have been fluorinated to the volatile uranium and plutonium products if the fines had been effectively returned to the fluidized bed for the recycle-fluorination.

With 1200 g of alumina as a basis for calculation, the final bed concentrations of 0.009 w/o plutonium and 0.009 w/o uranium correspond to less than 0.01% of the uranium and 1% of the plutonium charged to the reactor.

Table VIII lists some of the properties of the alumina bed after each batch of pellets was processed. After the first run, the specific surface area of the alumina bed increased by 0.12 sq m/g, followed by increases of 0.05 and 0.01 sq m/g after the second and third runs. Thus,

Figure 13 shows the plutonium content of fluidized alumina-bed samples taken during runs 19, 20, and 21. Note that an additional hour at 550°C in each of runs 19 and 20 would have probably reduced the plutonium to 0.009 w/o, as was done in run 18 (Fig. 10) and again in run 21. Effectively, then, the plutonium was maintained at the same level after each batch of fuel pellets was processed. Uranium concentrations in the fluidized beds for runs 19, 20, and 21 are given in Figs. B.19, B.20, and B.21 in Appendix B.

The fluidized-bed samples taken at 17 and 19 hr of process time in run 21 showed that the plutonium content in the fluidized bed reached a steady value of 0.009 w/o during recycle-fluorination at 550°C. A riffled sample of the final 615-g alumina bed, removed from the reactor, had a plutonium content of 0.012 w/o. This increase was probably due to fines falling

the increase in specific surface area was less than 5% after a third batch of pellets had been processed in the alumina bed. This result, obtained with Alcoa T-61 alumina, is in good agreement with the results of previous experiments,⁷ which used Norton, high-purity Blue Label Alundum.

TABLE VIII. Properties of an Alumina Bed Used to Process Several Batches of Simulated Fuel Pellets

Batches of Fuel Pellets Processed	Specific Surface Area, ^a sq m/g	Fluorine, w/o	Al ₂ O ₃ Converted to AlF ₃ , w/o	Uranium, w/o	Plutonium, w/o
0	0.05	-	-	-	-
1	0.17	2.33	2.0	0.009	0.013
2	0.22	3.43	2.8	0.009	0.012
3	0.23	4.42	3.6	0.009	0.009

^aBET measurement.

The fluoride content of the alumina bed increased from 2.33 w/o after processing the first batch of pellets to 4.42 w/o after processing the third batch of pellets; this result is also in good agreement with the previous experiments. If an allowance is made for the presence of uranium, plutonium, and nonvolatile fission-product fluorides, the alumina converted to aluminum fluoride increased from 2.0 w/o after the first run to 3.6 w/o after the third run at an average linear increase of 0.8 w/o per batch of pellets processed. These results for T-61 alumina were about 12% higher than those observed in the previous experiments⁷ for the initial three runs with the same batch of Alundum. Although the specific surface areas and alumina converted to aluminum fluoride showed a relatively high rate of change from run 19 to run 21, the absolute magnitudes are still relatively low, indicated that increased surface area and fluorination of the alumina should pose no problems in the reuse of the alumina-bed material.

Runs 19, 20, and 21 have demonstrated that the reuse of a single batch of alumina to process several batches of pellets is a promising method of minimizing total plutonium losses and reducing the quantity of solid wastes from a fluid-bed fluoride-volatility process. Although this principle had been demonstrated in previous alumina reuse experiments,⁷ the present tests are more nearly representative of actual processing conditions because they were carried out with simulated fuel pellets containing a larger group of fission products. In addition, a relatively economical, commercial form of alumina rather than the more costly, high-purity Alundum was used in these tests. Further, to process three batches of fuel pellets as in runs 19, 20, and 21 a total recycle-fluorination time of 33 hr is recommended; this time is about half the 60 hr of recycle-fluorination used in the previous tests.

F. General Process Considerations

1. Plutonium Material Balances

Although the demonstration of material balances was not the purpose of the experimental program, several methods of completing a plutonium material balance were attempted during these experiments. Table IX lists the methods used and results obtained. Each of the four methods was used in the two-zone oxidation-fluorination experiments (runs 1 to 16), but only Method IV was used for runs 17-22. In each method, two 100°C sodium fluoride traps in series (see Fig. 1) were used as the final backup traps for hexafluoride collection.

TABLE IX. Plutonium Material Balances

Runs 1-16 Two-zone oxidation-fluorination
Runs 17-22 Separate oxidation and fluorination steps

Run	Nominal ^a Pu Charge, g	Plutonium Balance, %	Samples ^b Accounting for Most of Pu Product
1	2.8	32	I
2	2.8	32	I
3	2.8	47	I
4	2.8	24	II
5	2.8	14	II
6	2.8	72	II
7	2.8	19	II
8	2.8	59	II
9	2.8	34	II
10	2.8	12	II
11	1.4	44	III
12	2.8	56	III
13	5.6	44	IV
14	2.8	52	IV
15	3.1	69	IV
16	2.8	84	IV
17	2.8	114	IV
18	2.8	89	IV
19,20,21	8.4	96	IV
22	2.8	93	IV

^aFor runs 1-6, Type I pellets were used; for all other runs, Type II pellets were used.

^bMethod I, liquid hexafluoride sample; Method II, liquid hexafluoride sample and 300°C NaF trap; Method III, liquid hexafluoride sample and 100°C NaF; Method IV, 100°C NaF only (see text).

In Method I, about 800 g of UF_6 - PuF_6 mixture was collected during a run in the three cold traps at $-78^\circ C$. After each run, the condensed hexafluorides were transferred from the cold traps and consolidated into a single sampling cold trap, which was then inverted and placed in position on the sampling manifold as shown in Fig. 14.

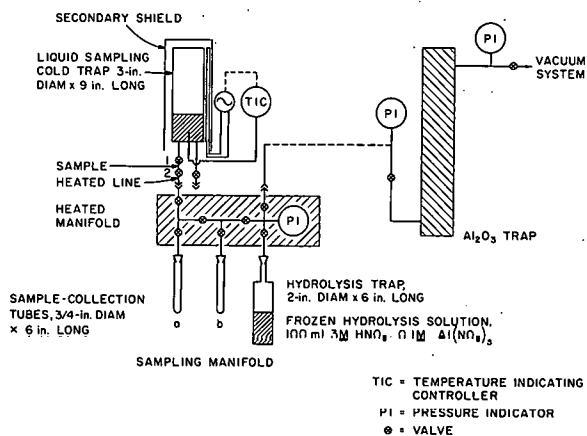


Fig. 14. Schematic Diagram of Sampling Manifold for Liquified Uranium and Plutonium Hexafluoride Products

The hexafluorides were heated to $70^\circ C$ to collect approximately 10 g of liquid sample in a 2- to 3-cc sample volume located between the valves 1 and 2 shown in Fig. 14. The sample was then transferred to collection tube a, and subsequently tube b was used to collect a duplicate sample. Hexafluoride samples from the collection tubes were transferred by vaporization to the hydrolysis trap which contained 100 ml of

frozen ($-78^\circ C$) hydrolysis solution, 3 to 6M HNO_3 -0.1M $Al(NO_3)_3$. Hydrolysis of the hexafluoride samples took place as the trap slowly warmed to ambient temperature.

For Method II, the first of the three cold traps used for product collection during the run was replaced by a 2-in.-diam, 6-in.-high NaF trap, held at $300^\circ C$. At this temperature, UF_6 would pass through the trap while PuF_6 would be removed from the gas stream.²¹ Hexafluoride products collected in the cold traps were sampled as described above.

For Methods III and IV, the $300^\circ C$ NaF trap was not used. The cold traps were used only when most of the UF_6 was being formed during fluorination with low concentrations of fluorine, and when most of the plutonium product was collected on the $100^\circ C$ NaF backup traps during the recycle-fluorination. In Method III, liquid hexafluoride samples were taken from the cold traps; in Method IV, these cold traps were not sampled.

As shown in Table IX, all four methods of obtaining a plutonium material balance were used for the two-zone experiments (runs 1-16). In particular, the major problems with obtaining a good plutonium balance appeared to be associated with the sampling of the liquified UF_6 - PuF_6 product. Normally, a U/Pu ratio in the product of approximately 200 was expected; in practice, ratios of 10^3 to 10^4 were obtained. While the α -decomposition of PuF_6 to solid PuF_4 at rates up to 2% per day^{10,22} would affect the U/Pu ratio, this correction was insignificant in accounting for U/Pu ratios of 10^3 or more in hydrolyzed samples.

Plutonium material balances were not improved appreciably by installing the 300°C NaF trap in front of the cold traps. Because this trap was relatively small, the gas had a rather short residence time, less than 0.5 sec, and some of the NaF may have been bypassed. Thus, a heavy dependence upon sampling of the liquified product remained.

Material balances based upon liquid samples of the hexafluoride products were affected by decomposition of the products to solid compounds, as shown by the data in Table X. The solids recovered from the various containers contained more plutonium than can be attributed to an α -decomposition rate of 2% per day. In addition, about twice as much UF₆ as PuF₆ decomposed in the collection vessels. X-ray fluorescence scans of the solids from cold trap No. 2 and from the liquid-sampling cold trap indicated major concentrations of uranium and plutonium plus intermediate concentrations of molybdenum and ruthenium. Liquid samples of the hexafluoride product taken after run 2 indicated that about 37% of the molybdenum and less than 8% of the ruthenium charged to the reactor were collected in the product cold traps. Thus the major constituents* in the product cold traps were also found in the solid residue from decomposition of the volatile fluorides.

TABLE X. Composition of Recovered Solids from Selected Hexafluoride Product Containers

Vessel	Total Solids, g	Uranium		Plutonium		U/Pu
		w/o	g	w/o	g	
Sample collection tubes a and b	0.125	33.0	0.041	19.8	0.025	1.6
Cold trap, No. 2 ^a	10,341	23.5	2.43	8.5	0.88	2.8
Liquid sampling cold trap	6,040	36.1	2.18	20.8	1.26	1.7

^aCenter cold trap in hexafluoride collection system shown in Fig. 1.

The material balance for plutonium, which includes the solids shown in Table X, was 63% for the entire set of experiments (runs 1-22). When sampling of liquid hexafluoride products was avoided by collecting most of the plutonium product on NaF at 100°C (runs 13-22), the average plutonium balance improved to 79%. A further improvement was recorded when separate oxidation and fluorination steps were used, allowing a more positive channeling of more of the PuF₆ product to the NaF trap. For these experiments (runs 17-22), the average plutonium balance was 97%.

*Rhodium and niobium also form volatile fluorides; however, analytical methods of detection for rhodium were not available, and niobium content in the pellets was only 1 ppm.

The sampling procedure for the sodium fluoride, the major source of plutonium product in runs 17-22, was examined and evaluated. In the sampling procedure, 1/8-in.-diam by 1/8-in.-high sodium fluoride pellets from the top half* of the trap were reduced in size in a disk mill. The sodium fluoride was then riffled several times to reduce the sample size to about 10-20 g. For the evaluation tests, the initial sample was

TABLE XI. Analytical Results for Duplicate Samples Taken from Sodium Fluoride Traps

Run	Sample	Uranium, w/o	Plutonium, w/o
19	1	11.6	0.095
	2	11.9	0.095
20	1	8.7	0.125
	2	8.5	0.34
21	1	12.1	0.132
	2	11.9	0.133
22	1	13.2	0.099
	2	13.3	0.104

obtained in this manner and the remaining sodium fluoride was recombined, mixed, and riffled once again to obtain a second sample. Table XI shows the analytical results obtained in these tests.

The plutonium analysis for the duplicate sample from run 20 is obviously in error. In this case, 2.1 kg of NaF was sampled and the analysis indicates that more than 7 g of plutonium was present in the trap, whereas only 2.8 g of plutonium was charged to the reactor for the run. The reason for this spurious result has not been determined. For each of the other duplicate analyses,

however, the average deviation for the uranium analyses was 0.2 w/o, and for the plutonium, 0.002 w/o. These results are within the precision of the analytical techniques, which have standard deviation of 2%, and indicate that a representative sample of the sodium fluoride was obtained by the sampling method.

The demonstrated plutonium material balance of 97% for runs 17-22 can be further improved by including the plutonium in the fines that remained in the uppermost parts of the reactor filters and the filter section and were not recovered by rapping and brushing the reactor after each run. Over 36 runs with plutonium pellets, an average of 1.6% (about 0.045 g) of the plutonium charge per run accumulated in these fines.²³ This discussion illustrates that good plutonium material balances can be obtained on a routine basis in operational equipment, provided that adequate collection and sampling techniques are used.

2. Plutonium Inventory in the Reactor

In addition to the fines inventory contained on the filters and in the filter section of the reactor (see Section IV.F.1 above), an average of 6.6 g of fines was recovered after each run by vigorous rapping and by brushing most of the interior surface of the reactor disengaging and filter

*In previous sampling tests, only trace amounts of plutonium were found in the bottom half of the NaF trap.

sections. (The reactor disengaging section operated at 150-500°C, and the filter section at 70-280°C.) These fines contained an average of 0.07% of the uranium charge and 3.4% (0.096 g) of the plutonium charge. Thus the total fines inventory in the upper sections of the reactor contained an average of 5% (0.14 g) of the plutonium charge. As discussed below, the plutonium contained in these fines probably represented a process holdup or a reactor inventory rather than a process loss.

That these fines did not freely return to the alumina bed after each run, where the plutonium might then be considered a process loss, is shown by the plutonium contents in samples of the final alumina bed taken after each run. Since the major objective of these experiments was to determine fluorination conditions required to minimize residual plutonium (and uranium) in the alumina fluidized bed, two samples of the final alumina bed were taken after each run. One sample was taken while the bed was still fluidized, and the second sample was obtained by riffling the alumina bed recovered from the reactor.

The reactor was jostled and vibrated during the removal of the fluid-bed section, and any loose material from the upper sections of the reactor would be expected to fall back into the static alumina bed. As shown by the following data, this was not the case.

In all experiments, uranium removal from the alumina bed was 99.9% of the charge so that only the plutonium in the final bed samples was of primary interest. Table XII lists the plutonium contents of the

TABLE XII. Comparison of Plutonium in Final Alumina Beds: Fluidized-bed Samples and Riffled Samples from Static Beds

Run	Plutonium Concentration $\times 10^3$		
	Fluidized Bed, w/o	Static Bed, ^a w/o	Fluidized - Static, w/o
1	7.0	6.3	0.7
2	6.8	6.9	-0.1
3	7.6	15.2	-7.6
4	4.7	5.3	-0.6
5	7.2	7.2	0
6	7.4	6.2	0.8
7	18.0	17.4	0.6
8	14.0	14.0	0
9	21.0	21.0	0
10	11.0	12.0	-1.0
11	10.0	10.0	0
12	6.0	6.0	0
13	23.0	25.0	-2.0
14	7.0	9.0	-2.0
15	29.0	25.0	4.0
16	31.0	34.0	-3.0
17	8.0	10.0	-2.0
18	10.0	9.0	1.0
19,20,21 ^b	9.0	12.0	-3.0
22	8.0	9.0	-1.0

^aRiffled samples.

^bAlumina reuse experiments.

two samples taken after each run. The average difference in the plutonium content of the fluidized- and static-bed samples was -7.6×10^{-4} w/o, and the standard deviation of this mean was 5.05×10^{-4} w/o. These statistics indicate that, on the average, the mean difference between samples is contained in the range $+0.3 \times 10^{-3}$ to -1.8×10^{-3} w/o plutonium for the 95% level of confidence, and the plutonium content of both the fluidized- and static-bed samples adequately represented the plutonium content of the entire alumina bed. Therefore, the total plutonium holdup in the reactor was represented by the plutonium contained in the fines remaining on the interior walls and filters of the reactor after each run.

Plutonium in the fines remaining in the reactor can be fluorinated to the volatile hexafluoride if the fines are efficiently returned to the reaction zone during the recycle-fluorination period. This was demonstrated in boat-reactor experiments²³ in which, the plutonium content of the fines material that was collected after several runs was subjected to the recycle-fluorination sequence used in the runs. The plutonium concentration in this material was reduced from 6.7 to 0.2 w/o or to a final plutonium content that represented only 0.4% of the plutonium charge. Additionally, the fines could be fluorinated in situ in the reactor if the fluid-bed equipment were specifically designed for this purpose, as demonstrated by the cleanup fluorinations carried out in pilot-plant equipment.¹⁸

Since plutonium in the fines remaining in the reactor can be effectively recovered, this plutonium is not considered to be a process loss. It is desirable, however, to reduce the total plutonium content of these fines, and various methods have been investigated in the development of an alternative process--the interhalogen fluoride-volatility process.²⁴

3. Agglomeration of Alumina-bed Material

About 10% of the alumina bed was agglomerated during the first three experiments with plutonium-containing fuel pellets. In these runs, a corrosion specimen-holder with six attached coupons was present in the reactor; initially, it was thought that the holder produced regions with little solids movement in the fluidized bed and contributed heavily to the agglomeration. Consequently, in all subsequent runs the specimen holder was withheld from the reactor. However, in run 4, approximately 45% of the final alumina bed of 903 g agglomerated, indicating that the specimen holder was not the main factor contributing to this problem. Fluid-bed samples taken during runs 1-4 indicated that small clusters of five to eight alumina particles began to appear after 1-2.5 hr of the initial recycle-fluorination period. In these runs, a fluorine feed of 2 liters/min was used to place the system on recycle, but the reactor was generally not rapped to return elutriated fines to the fluidized bed before the start of recycle-fluorination. Based on measurements taken

with the thermal-conductivity cell, we estimated that the fluorine concentration increased to 90 v/o in 20 min when the system was put on recycle with 2-liters/min fluorine feed. In the early stages of recycle-fluorination, local temperature excursions may have been caused by accelerated reaction of high concentrations of fluorine with reactive fines that were returned to the bed by rapping the disengaging and filter sections of the reactor. These temperature excursions probably caused agglomeration of some of the alumina-bed material.

To avoid the formation of agglomerates, we modified operational procedures for increasing the fluorine concentration at the beginning of recycle-fluorination and for controlling the return of fines to the bed. Beginning with run 6, a lower fluorine flow rate of 0.5 liter/min was used and the reactor was rapped at frequent, regular intervals (see Section III.C.6). With 0.5-liter/min fluorine feed, 70 v/o fluorine was reached in 45 min; the fluorine feed was then increased to 2 liters/min to raise the fluorine concentration to 90 v/o. The modified procedure was effective; no agglomeration of the alumina was encountered in run 6 and subsequent runs. Agglomeration of the alumina-bed material is not expected to be a processing problem under controlled fluorination conditions.

4. Attrition of Alumina-bed Material

Diminution of the alumina-bed particles by attrition during fluidization and by chemical reaction during fluorination was measured for a variety of processing conditions. Before each test, the -170 mesh fraction was removed from the starting bed of alumina; Table XIII summarizes typical results. The 24-hr fluidization test in a plastic mockup of the 2-in.-diam reactor showed that 4.4 g in 1100 g or 0.4% of the alumina bed attrited to less than -170 mesh by fluidization alone.

TABLE XIII. Attrition of Alumina during Experiments in a 2-in.-diam Fluid-bed Reactor

Starting Bed Material: Alcoa T-61 Tabular alumina,
nominal 48 to 100 mesh
(-170 mesh fraction removed)

Run No.	Type of Fuel Pellets	Reaction Conditions ^a		Final Alumina Bed (% less than 170 mesh)
		Temperature Range, °C	Time, hr	
_b	-	~25	24.0	0.4
C	UO ₂	450-550	23.5	1.1
8	UO ₂ -PuO ₂ -F.P.	450-550	12.0	0.6
9	UO ₂ -PuO ₂ -F.P.	450-550	24.0	0.8
18	UO ₂ -PuO ₂ -F.P.	350-550	16.0	1.0
19,20,21	UO ₂ -PuO ₂ -F.P.	350-550	51.0	1.0

^aDetailed operating conditions are presented in Appendix A.

^bAlumina-bed material was fluidized in a plastic mockup of the 2-in.-diam fluid-bed reactor at room temperature.

In addition to attrition of the alumina by fluidization, a 650-g batch of $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets adds about 5 g of nonvolatile fission-product fluorides fines, which correspond to 0.45% of an 1100-g bed of alumina. Additionally, fine powders are recovered from the upper parts of the reactor by rapping and brushing after each experiment. For the entire series of runs using 22 batches of $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets and 20 batches of alumina, an average of 7.5 g of fines per batch of alumina were recovered from the upper parts of the reactor. This result, in addition to the 1% -170 mesh found in the alumina beds (see Table XIII) and the fines resulting from the pellets, indicates that the total diminution of alumina caused by fluidization and reaction was about 1% per run. Similar results have been obtained in pilot-plant studies²⁵ with a 6 in.-diam fluid-bed reactor in which uranium alloy fuels were processed by fluoride-volatility methods. In these studies, about 1% of the sintered, nominal 28 to 100 mesh alumina bed was attrited and carried over to a packed-bed filter in each run. For the pilot-plant tests, a typical processing sequence consisted of chlorination for 6 hr at 350-370°C with HCl, fluorination for 2 hr at 350°C with HF, and then fluorination for 6 hr at 250-500°C with fluorine.

For the alumina reuse experiment (runs 19-21), 1% of the final bed, corresponding to 12 g of fines in 1200 g of alumina, was less than 170 mesh and 23.4 g of fines were recovered from the upper parts of the column, for a total of 35.4 g of fines. Of this total, about 15 g of fines could be attributed to nonvolatile fission-product fluorides from the pellet charges. Evidently, then, about 1.7% of the original 1200 g of alumina attrited to -170 mesh after three uses of the alumina. Diminution of the alumina bed to this extent did not noticeably affect fluidization of the bed and is not considered to be a processing problem.

5. Distribution of Uranium, Plutonium, and Fission Products in Screened Fractions of the Alumina Bed

The concentrations of uranium, plutonium, and selected fission products in particle-size fractions were obtained from samples of the final alumina beds for three runs in which UO_2 pellets, Type I $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets, or Type II $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ pellets with cesium fluoride added to the alumina bed, were processed. Results are presented in Table XIV.

TABLE XIV. Concentrations of Uranium, Plutonium, and Selected Fission Products in Screened Fractions of Alumina Beds

Charge to Reactor: ~650 g of fuel pellets
1100 g of alumina
0.6 g of CsF (Run 8 only)

Mesh Size	Average Particle Size, μ	UO_2 Pellets (Run B) ^a U, w/o	Type I $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ Pellets (Run 2) ^a					Type II $\text{UO}_2\text{-PuO}_2\text{-F.P.}$ Pellets, CsF Added (Run 8) ^a		
			U, ^b w/o	Pu, ^b w/o	Sr, w/o	Y, w/o	Zr, w/o	U, ^b w/o	Pu, ^b w/o	Cs, w/o
-40 +60	335	0.003	0.0024	0.009	0.012	0.008	0.062	0.016	0.011	0.048
-60 +80	214	0.002	0.0024	0.006	0.011	0.009	0.068	0.017	0.014	0.040
-80 +120	151	0.004	0.0025	0.006	0.016	0.012	0.083	0.019	0.016	0.043
-120 +170	107	0.006	0.0031	0.009	0.018	0.014	0.084	0.021	0.016	0.045
-170 +325	66	0.020	0.0108	0.054	0.015 ^c	0.031 ^c	0.235 ^c	0.019	0.018	0.084
-325	-	-	0.0178	0.049				0.56	0.042	0.097

^aDetailed run conditions are given in Appendix A.

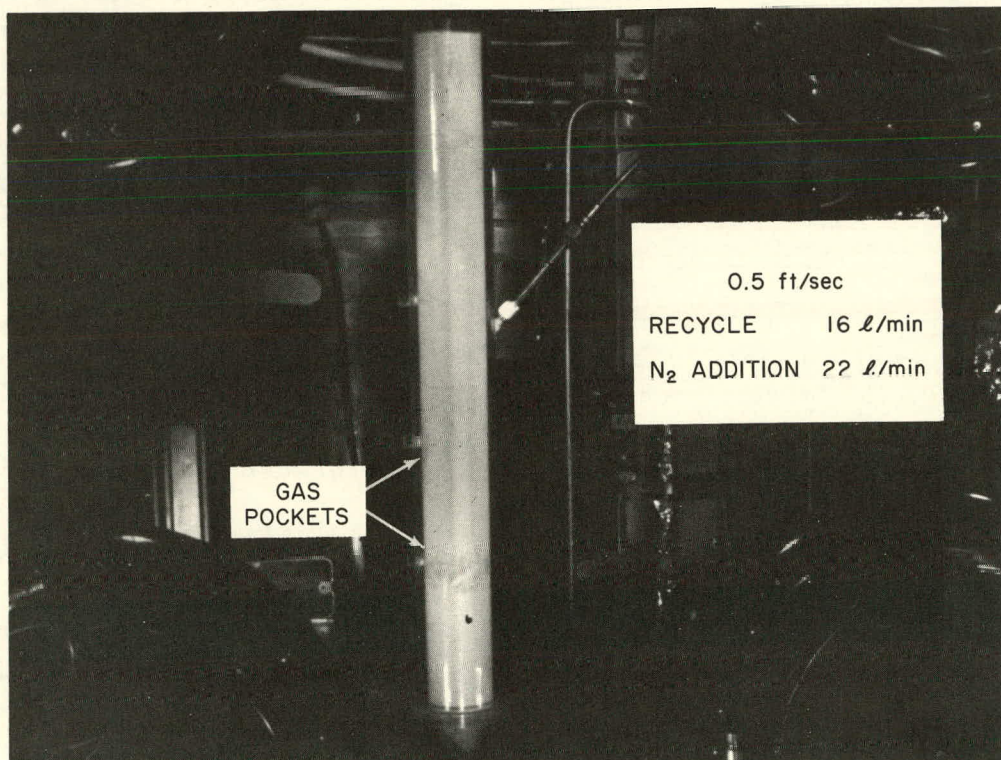
^bU and Pu analyses by wet chemical methods; Sr, Y, Zr, and Cs analyses by X-ray fluorescence methods.

^c-170 and -325 fractions combined to provide sufficient sample for analysis.

There was little variation in the concentrations of uranium, plutonium, and fission products for average particle sizes of 107-335 μ , but the concentrations increased significantly for particles less than 170 mesh (88 μ). The concentrations of uranium and plutonium in the -170 mesh material for run 2 with no cesium present were approximately six times those for the +170 mesh material; the concentrations of strontium, yttrium, and zirconium were about three times as high in the -170 mesh material than in the +170 mesh material. Similarly, the -325 mesh material from run 8 with added cesium contained more uranium, plutonium, and cesium than the larger particles. Since the -170 mesh material represented only about 1% of the final bed, as indicated in Section 4 above, the bulk of the uranium, plutonium, and fission products was associated with the coarser alumina particles.

6. Quality of Fluidization under Gas-recycle Conditions

Since a pulsating gas flow was produced by the remote-head diaphragm pump used to recirculate the fluorine during recycle-fluorination, the behavior of a fluidized alumina bed was examined under these conditions. A Lucite fluid-bed section was attached to the metallic disengaging and filter sections, and nitrogen at room temperature was recycled by the pump under simulated processing conditions. Figure 15 is a frame from a



308-599A

Fig. 15. Fluidization of an Alumina Bed Using Recycled Gas at Ambient Temperature

motion-picture film of the 1100-g bed of fluidized alumina under conditions of recycled gas flow. Almost stationary pockets of gas were observed at two positions in the alumina bed under processing conditions, and these were presumably related to the pulsation of the gas flow. Good solids movement was observed in these tests even though a pulsation effect was imposed on the fluidized bed, and it was concluded that fluidization quality during recycle-fluorination was satisfactory.

7. Leaching of Alumina Beds for Plutonium Recovery

Several experiments were performed to determine the feasibility of recovering plutonium by leaching the alumina fluid-bed material after most of the uranium has been removed by fluorination with fluorine. This process alternative is not considered as an integral step in the all-volatility process concept, but was investigated to demonstrate the added versatility in the plutonium-removal step when most of the uranium has been fluorinated with fluorine at a relatively low temperature.

In these experiments, samples of the alumina fluid-bed material were taken in run 18 after 2 hr of pellet fluorination at 350°C with 16 v/o fluorine. The samples were leached with 6N nitric acid for 2, 3, or 5 hr at 100°C. Table XV compares the results from these leaching tests with the initial sample as well as a control sample. These tests indicate that 99.5% of the residual uranium and plutonium can be readily leached from the alumina after a short-term, low-temperature exposure to fluorine.

TABLE XV. Leaching of Alumina-bed Samples Following Fluorination of Oxidized UO₂-PuO₂-F.P. Pellets with 16 v/o Fluorine at 350°C for 2 hr during Run 18

Leach Solution: 6N HNO ₃ Temperature: 100°C				
	Sample No.	Leaching Time, hr	Uranium, w/o	Plutonium, w/o
Original Sample	-	-	0.088	0.164
Leached Samples	1	2	0.0011	0.00041
	2	3	0.003	0.0083
	3	5	0.0005	0.00029
As-received Al ₂ O ₃	Blank	3	0.00019	0.00007

Sample	Uranium		Plutonium	
	Percent Leached ^a	Material Balance, ^a %	Percent Leached ^a	Material Balance, ^a %
1	98.9	101.0	99.8	104.4
2	97.1	96.2	95.1	84.4
3	99.5	92.6	99.8	94.2

$$^a\% \text{ Leached} = 100 \left(1 - \frac{M_{\text{solids}}}{M_{\text{solids}} + M_{\text{soln}}} \right)$$

$$\text{Material Balance} = 100 \frac{M_{\text{solids}} + M_{\text{soln}}}{M_{\text{original sample}}}$$

where M = weight of plutonium or uranium, and solids correspond to leached alumina samples.

8. Use of Thermal-conductivity Cell to Monitor Uranium Fluorination

As outlined in Section III.B above, the thermal-conductivity cell was used to continuously monitor the reactor off-gas for fluorine content during the two-zone oxidation-fluorination step, the single-zone fluorination step, and fluorination of the pulverized pellets. In these fluorination steps, low concentrations of fluorine were fed to the reactor to react the uranium, and high utilization of fluorine was possible. Thus, the thermal-conductivity measurements were able to provide significant information concerning the fluorine utilization and the rate of reaction for the major species (uranium) during several important steps in the processing cycle.

Let us assume that all the fluorine consumed in the reactor appears as the most significant volatile product, UF_6 , and that formation of solid, intermediate uranium, plutonium, and fission-product fluorides is negligible. Then the rate of UF_6 production and the utilization of fluorine to form UF_6 can be calculated from the thermal-conductivity measurements. These calculations have been carried out and are plotted in Fig. 16 for the

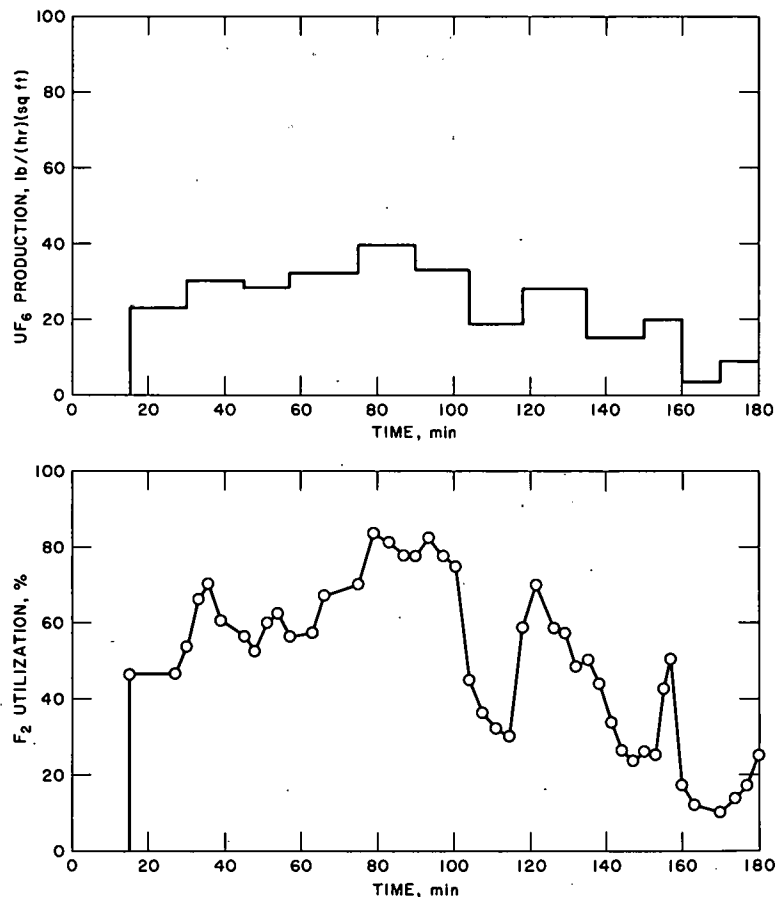


Fig. 16. Uranium Fluorination during Two-zone Oxidation-Fluorination of Fuel Pellets in Run 3 as Determined from Continuous Thermal-conductivity Measurement of Reactor Off-gas

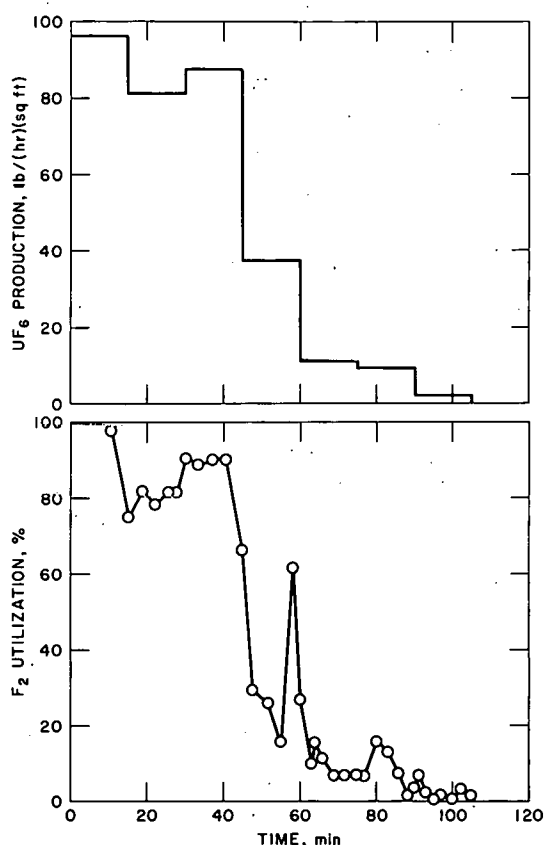


Fig. 17. Uranium Fluorination from Pulverized Fuel Pellets in Run 18 as Determined from Continuous Thermal-conductivity Measurement of Reactor Off-gas

minimum rate of 19 lb/(hr)(sq ft). The fluorine utilization increased to more than 80% after 80 min of operation and then generally decreased to a low of 10% after 170 min of operation.

An induction period was not observed in run 18 for the fluorination of uranium from the pulverized pellets. The highest rates of reaction, 97 lb of UF_6 per (hr)(sq ft), were obtained at the start of reaction and were limited only by the rate of fluorine feed. As shown in Fig. 17, the reaction rate was high during the first hour of operation and then decreased as a function of time, which is typical of batch reactions. The fluorine utilization in run 18 was 100% for the first 10 min and greater than 80% for the first 80 min.

Both Figs. 16 and 17 indicate that the assumption of a steady-state reaction, such as that shown by the averaged UF_6 rates, does not completely represent the reaction of U_3O_8 with fluorine. The fluorine utilization curves, which more closely approach a differential method of observing the reaction rate, indicate that the actual rate may vary widely although the generally increasing and decreasing rate periods are clearly observed.

two-zone oxidation-fluorination step of run 3 and in Fig. 17 for the fluorination of uranium from pulverized pellets in run 18. In these runs, the quantity of hexafluoride product was measured at the end of the time periods shown on the figures so that the calculations could be independently verified.

The thermal-conductivity data show that the two methods of processing a batch of fuel pellets provide an interesting contrast in both the production rates for UF_6 and the utilization of fluorine.

For the two-zone oxidation-fluorination step outlined in Fig. 16, an induction period of 15 min is evidenced before any uranium began to fluorinate. This result is similar to observations made in pilot-plant studies with UO_2 pellets.² Once the U_3O_8 began to fluorinate, however, the rate of production for UF_6 was relatively constant at about 30 lb/(hr)(sq ft) with a maximum rate of 40 and a mini-

For the reaction periods shown in Figs. 16 and 17, Table XVI compares the average rate of UF_6 production and the average fluorine utilization as calculated from actual operating data and from the thermal-conductivity measurements. The agreement between the rates of UF_6 production is very good for the two independent methods of calculation. For the fluorine utilization, the known fluorine-input rate must be used in both methods of calculation; however, the final results are also independently obtained and provide a second check on the thermal-conductivity data, which are again in good agreement with the experimental data.

TABLE XVI. Comparison of Average Production Rates and Fluorine Utilization Calculated from Experimental Data and from Thermal-conductivity Measurements

	<u>Run 3</u>	<u>Run 18</u>
<u>UF_6 Production, lb/(hr)(sq ft)</u>		
From weight of hexafluoride collected	22.0	38.5
From off-gas thermal-conductivity measurements	22.7	40.8
Deviation, %	-3.2	-6.0
<u>Fluorine Utilization to Form UF_6, %</u>		
From weight of hexafluoride collected and fluorine input	44.9	38.3
From off-gas thermal-conductivity measurements	46.2	40.1
Deviation, %	-2.9	-4.7

As Table XVI shows, the results from the thermal-conductivity data are higher than the experimental data by 3-6%. There are reasons to anticipate that the agreement is actually much better than reported here. For example, two fluorine utilizations may be calculated:

$$1. (F_2 \text{ Utilization})_1 = \frac{3 \times \text{moles hexafluoride collected}}{\text{Total moles fluorine fed}} \times 100.$$

$$2. (F_2 \text{ Utilization})_2 = \frac{\text{Total moles fluorine consumed}}{\text{Total moles fluorine fed}} \times 100.$$

The latter fluorine utilization includes all the fluorine consumed to form the volatile hexafluoride products plus the fluorine used in forming solid, intermediate uranium and plutonium fluorides, fission-product fluorides, and aluminum fluoride in the alumina bed. This second fluorine utilization is the one actually calculated from the thermal-conductivity data and, as indicated by the above equations, this utilization

will always be higher than or equal to the utilization of fluorine to form the hexafluoride products. Thus, the results calculated in Table XVI indicate that approximately 3-5% of the fluorine feed reacted to form fluorides other than the volatile hexafluoride products during the run periods outlined.

In Section IV.D.1, it was shown that the thermal-conductivity data for run 17 could be used to calculate reaction-rate constants when the uranium content of the fluidized bed was known as a function of time. Similar calculations could not be made for runs 3 and 18 because bed samples were not taken during the time periods shown in Figs. 16 and 17 and because the rate of UF_6 production was not measured as a function of time. However, data in the figures could be used to estimate rate constants according to the diminishing-sphere model. For the two-zone step in run 3, two rate constants were calculated: from 30 to 75 min, $k' = 3.0 \times 10^{-3} \text{ min}^{-1}$; and from 85 to 150 min, $k' = 5.4 \times 10^{-3} \text{ min}^{-1}$. For run 18, during fluorination of uranium from the pulverized pellets at 350°C , a rate constant of $8.0 \times 10^{-3} \text{ min}^{-1}$ was obtained; this result was in agreement with similar data from run 17.

9. Statistical Analysis of Experimental Data

Experimental data and operational parameters from runs 1-14 were statistically analyzed to determine the effects of process variables on the rate of removal of plutonium during recycle-fluorination and on the final plutonium content of the fluidized bed. Since the available data were inadequate for a complete statistical analysis, empirical correlations relating plutonium removal to the operating conditions were not sought. The two methods used to analyze the data were as follows:

a. Method 1. A stepwise multiple-regression technique was used to relate plutonium concentration in the alumina bed after each step in the reaction sequence to the operating variables in order to identify the variables with significant effects. An available computer program²⁶ was modified for use on a CDC-3600 computer to calculate correlation coefficients that gave an estimate for the apparent association between two variables and the partial regression coefficients which corresponded to the equation

$$y = a + bx + cx_2 + dx_3 + \dots$$

At each step in the stepwise regression, the variable that gave the greatest improvement in the "goodness of fit" was added to the regression equation.

The dependent variable used for the calculation was the negative logarithm of the plutonium concentration. The log function was used so that equal percentage deviations about the fitted regression line

would be weighted uniformly. The use of the actual values in the regression analysis would have resulted in greater significance being attached to high plutonium concentrations compared with low concentrations. Thus, with the log function the data were fitted to an equation of the form

$$y = A \exp(bx_1 + cx_2 + dx_3 + \dots).$$

b. Method 2. Empirical equations were fitted to the individual curves of plutonium concentration as a function of time during recycle-fluorination at 450, 500, and 550°C. Appropriate constants in these equations were then analyzed in terms of the process variables. A plot of the logarithm of the plutonium-removal rate versus time gave an approximate linear relationship with negative slope for each recycle-fluorination period in a given run.

Hence,

$$\log \frac{dy}{dt} = -kt + C,$$

where y = plutonium concentration in alumina bed at time t , and k and C are constants. Taking antilogarithms and integrating leads to

$$y = Ae^{-kt} + B,$$

where A and B are constants that can be calculated in terms of given limits. For the limits,

$$y = y_i \text{ for } t = 0,$$

and

$$y = y_e \text{ for } t = \infty.$$

The equation becomes

$$\frac{y - y_e}{y_i - y_e} = e^{-kt}.$$

A least-squares analysis²⁷ was performed by computer to obtain the best fit of this equation to the curves of plutonium concentration versus time for each recycle-fluorination period. Note that k is a characteristic of the rate of plutonium removal, whereas y_e represents the limiting plutonium concentration that can be obtained for a given set of operating conditions. Values of y_e and k (as the log function) for recycle-fluorination at

500 and 550°C were then analyzed in terms of the operating variables, as in Method 1. The analysis was not carried out for recycle-fluorination at 450°C because of insufficient data.

The advantage of Method 2 is that it uses an improved model relating changes in plutonium concentration with time, i.e., the rate of plutonium fluorination. Thus the analysis provides information relating the effects of the operating variables on the rate of plutonium volatilization, as well as on the residual plutonium content in the alumina bed.

Correlation coefficients and partial-regression coefficients did not necessarily indicate the same variables to be significant. This results from the different criteria involved in the calculation of the two coefficients. The correlation coefficient gives an estimate of the apparent association between two variables, but does not take account of possible interaction of other variables. The partial-regression coefficient describes the effect of an "independent" variable while all other variables are held constant. Davies²⁸ discussed an equivalent situation in comparing total-regression coefficients and partial-regression coefficients. He pointed out that total-regression coefficients (and this applies to correlation coefficients also) may depend much more on the arrangement of the observations with respect to an independent variable than on any real effects of the factors concerned. For example, the final plutonium concentration in the alumina bed has generally been higher in later runs, compared with early runs, because of the addition of cesium fluoride in most of the later runs. In addition, bed pulsing was not used in early runs but has been used sparingly in later runs. Consequently, the correlation coefficient for bed pulsing indicated an effect of this variable on the final plutonium concentration; the apparent association of these variables is attributed to the arrangement of the observations, as described above. The inclusion of variables as significant at the 95% confidence level in the regression equation was considered to give a better indication of the significant variables in this work.

Some variables that might be expected to have important effects were shown to be insignificant. However, in many instances, variables have not been sufficiently changed relative to other variables to adequately separate their effects. For example, the available data suggested that significant correlations exist between the frequency of rapping the reactor, the duration of recycle-fluorination at 450, 500, and 550°C, the addition of cesium fluoride, and the use of Type II pellets, when actually these are independent variables. This indicates the need for the proper design of experiments if statistical methods of analysis are to be used.

The analyses showed that the residual plutonium following each recycle-fluorination step generally decreased with (1) a decrease in the starting plutonium concentration, (2) a decrease in the pellet-to-alumina

charge ratio, and (3) the omission of cesium fluoride from the alumina bed. The rate of plutonium removal from the alumina bed for recycle-fluorination at 500°C, as described by the rate constant k , was increased when Type II pellets were used, and, for recycle-fluorination at 550°C, k increased with a decrease in the duration of recycle-fluorination at 450°C.

The average UF_6 and PuF_6 production rates during two-zone oxidation-fluorination were included as variables in these analyses since previous work^{29,30} had indicated that uranium and plutonium retention was a function of the partial pressures of the hexafluorides during the main fluorination step. In the present work, the final plutonium concentration in the alumina bed had a significant correlation with both UF_6 and PuF_6 production rates, as indicated by the correlation coefficients. The rate of plutonium removal (k) during the 500 and 550°C recycle period did not show any correlation with UF_6 and PuF_6 production rates during the two-zone fluorination period.

V. SUMMARY

The fluorination of uranium and plutonium from a fluidized bed of alumina has been demonstrated in a 2-in.-diam fluid-bed reactor using simulated, spent-power reactor-fuel pellets containing UO_2 , PuO_2 , and nonradioactive fission-product oxides. The objectives of this study were to determine the fluorination conditions required to minimize the retention of uranium and plutonium in the alumina bed, which would be discarded as waste from a fluid-bed fluoride-volatility process.

Generally, the pellet-to-alumina charge ratio for an experiment was 0.6 and consisted of 1100 g of alumina and 650 g of pellets, which contained 560 g of uranium and 2.8 g of plutonium. The pellets were initially reacted by either a two-zone method of simultaneous oxidation and fluorination or by oxidation and fluorination in separate steps. The two-zone step was carried out at 450°C for 3 hr using 20 v/o oxygen and 10 v/o fluorine; in the separate oxidation and fluorination steps, the pellets were oxidized for 4 hr at 450°C with 20 v/o oxygen and then fluorinated with 5 to 16 v/o fluorine at 350°C for 2 hr. Operationally, both methods of processing the pellets were carried out on a routine basis. Approximately 80-100% of the uranium and about 20-75% of the plutonium in the pellet charge were reacted after the initial fluorination step. Further fluorination of plutonium required high concentrations of fluorine; thus the reactor off-gas was recycled to conserve the fluorine reagent. The recycle-fluorination step of the processing cycle used 90 v/o fluorine at 350 - 550°C for predetermined periods of time. The recycle-fluorination step was also carried out on a routine basis.

Pellets (Type II) made from physically mixed UO_2 , PuO_2 , and fission-product oxide powders reacted at greater rates during the two-zone oxidation-fluorination than pellets (Type I) made from solid-solution UO_2 - PuO_2 and fission-product oxides. Similar residual plutonium concentrations in the alumina bed were obtained with both types of pellets in experiments carried out under similar conditions.

Fission-product cesium was not present in either type pellet. Therefore, to simulate more closely the fission-product distribution that might exist in the reprocessing of irradiated fuel, cesium fluoride was added to the alumina bed for most runs. The addition of cesium fluoride to the alumina bed caused an increase in the plutonium remaining with the final alumina bed in experiments using the two-zone method of processing the pellets.

Plutonium material balances of 97% were routinely demonstrated in the 2-in.-diam reactor system when most of the UF_6 product was collected in cold traps during fluorination with 5-16 v/o fluorine at 350°C and most of the PuF_6 product was collected on NaF at 100°C during the recycle-fluorination with 90 v/o fluorine. Samples of liquified UF_6 - PuF_6 product

collected in cold traps during two-zone oxidation-fluorination experiments indicated that about 37% of the molybdenum and less than 8% of the ruthenium in the pellet charge was collected with the hexafluoride products. These results are consistent with the ANL reference flowsheet which anticipates a further separation of uranium and plutonium from the volatile fission-product fluorides.

The total plutonium holdup in the reactor, about 5% of the charge, was represented by plutonium contained in fines adhering to the interior walls and filters. These fines did not fall into the alumina bed when fluidization was stopped and were only recovered by vigorous rapping and brushing of the reactor or by scraping the filters and the upper filter section of the reactor. As demonstrated in boat-reactor tests, plutonium in the fines could be fluorinated to volatile hexafluoride if the fines were efficiently returned to the reactor during recycle-fluorination. Additionally the fines could be fluorinated in situ if the fluid-bed equipment were specifically designed for this purpose.

In the screened fractions of an alumina bed, the concentrations of uranium and plutonium in the -170 mesh material were approximately six times those for the +170 mesh material; similarly, the concentrations of strontium, yttrium, zirconium, and cesium were about three times as high. However, the -170 mesh material represented only 1% of a final alumina bed, and the bulk of the uranium, plutonium, and fission products was associated with the coarser alumina particles.

The feasibility of recovering plutonium from the alumina bed by aqueous techniques after most of the uranium had been fluorinated was determined in several leaching tests. Samples of an alumina bed were taken after the pulverized pellets were fluorinated with 16 v/o fluorine at 350°C for 2 hr. The samples were leached with 6N nitric acid for 2, 3, or 5 hr at 100°C. The tests showed that 99.5% of the residual uranium and plutonium could be readily leached from the alumina after a short-term, low-temperature exposure to fluorine.

A thermal-conductivity cell was used to continuously monitor the reactor off-gas for fluorine content during the two-zone oxidation-fluorination step, the single-zone fluorination step, and the fluorination of the pulverized pellets. These data provided information concerning the fluorine utilization and the rate of reaction for the major species, uranium, during several important steps in the processing cycle. During the two-zone step at 450°C, an induction period of about 15 min was observed before any reaction of fluorine was detected; after this period, the production rate for UF_6 was relatively constant at about 30 lb/(hr)(sq ft). Fluorine utilization increased to about 80% and then generally decreased as the batch of pellets was completely reacted. When the pellets were oxidized in a separate step, no induction period for the fluorination of uranium at 350°C was

observed. Initial rates of reaction for UF_6 were 97 lb/(hr)(sq ft) and were limited only by the fluorine feed rate. While most of the uranium reacted, fluorine utilization was 100% initially and above 80%. In 2 hr of operation, production rates for UF_6 and fluorine utilization averaged 22 lb/(hr)(sq ft) and 45%, respectively, during the two-zone step and 40 lb/(hr)(sq ft) and 39% during fluorination of the pulverized pellets. Additionally, a comparison of fluorine utilization calculated from thermal-conductivity data and from the collected hexafluoride products indicated that about 3-5% of the fluorine feed reacted to form fluorides other than the volatile hexafluoride products.

The fluorination of uranium from the pulverized pellets with low concentrations of fluorine was fitted to a diminishing-sphere reaction model which describes a reaction with surface-reaction rate controlling by the equation

$$(1 - F)^{1/3} = 1 - k't.$$

At 300°C, the rate constant, k' , was $0.76 \times 10^{-3} \text{ min}^{-1}$, and at 350°C, k' was $6.5 \times 10^{-3} \text{ min}^{-1}$; these results gave an apparent activation energy of 31 kcal/mole and were of the same order as results obtained in thermo-balance studies that used two different sources of uranium.

The diminishing-sphere model was also applied to the fluorination of plutonium during the recycle-fluorination step. In one run, a fit of the data to the model was obtained at 350 and 375°C giving an estimated rate constant of $0.55 \times 10^{-3} \text{ min}^{-1}$ at both temperatures. However, the diminishing-sphere model did not adequately describe the fluorination of plutonium during the later stages of the recycle-fluorination periods.

The experimental data and operational parameters for 14 runs were analyzed using a stepwise multiple-regression technique and a least-squares analysis to obtain the best fit of an empirical rate equation relating plutonium concentration versus time for each recycle-fluorination period. It was desired to identify the variables having significant effects; however, since the available data were limited and therefore inadequate for a complete statistical analysis, empirical correlations relating plutonium removal to the operating conditions were not sought. The statistical analysis showed that the residual plutonium following each of the recycle-fluorination steps generally decreased with a decrease in the starting plutonium concentration, the pellet-to-alumina charge ratio, and the omission of cesium fluoride from the alumina bed. The rate of plutonium removal from the alumina bed for recycle-fluorination at 500°C, as described by the empirical rate constant k , was increased when Type II pellets were used; for recycle-fluorination at 550°C, k increased with a decrease in the duration of recycle-fluorination at 450°C. The final plutonium concentration in the alumina bed had a significant correlation with UF_6 and PuF_6 production rates during the two-zone step as indicated by the calculated correlation coefficients.

In experiments using a pellet-to-alumina charge ratio of 0.6 and the two-zone method of operation, residual levels in the alumina bed of 0.003-0.010 w/o uranium and 0.006 to 0.010 w/o plutonium were routinely obtained using a recycle-fluorination sequence totaling 12-20 hr. These residual levels corresponded to less than 0.1% of the uranium and 2.4-3.9% of the plutonium charged to the reactor. However, when cesium fluoride was added to the alumina bed, residual plutonium in the bed increased by about a factor of three for similar recycle-fluorination sequences. With a pellet-to-alumina charge ratio of 0.6, an optimum recycle-fluorination sequence following the two-zone processing step appeared to be 1 hr at 450°C, 3 hr at 500°C, and 4-5 hr at 550°C. With this recycle-fluorination sequence, plutonium in the final alumina bed was reduced to 5.5% of the plutonium charge. In experiments using pellet-to-alumina charge ratios in the range 0.3-1.2 and the recommended recycle-fluorination sequence, residual plutonium in the alumina beds ranged from 4.7 to 7.5% of the plutonium charge.

When cesium was included in the fission products, separation of the oxidation and fluorination steps appeared to be more promising than the two-zone method of operation for eventual process use. The separate steps allowed greater flexibility in the choice of operating conditions when fluorinating the major species, uranium. By fluorinating the uranium at 350°C and starting the recycle-fluorination at 350°C, rather than at 450°C as was done in the two-zone step, we overcame the effect of added cesium on the plutonium retention in the alumina bed. The recommended recycle-fluorination sequence following separate oxidation and fluorination steps, was 3 hr at 350°C, 6 hr at 350-550°C and 1 hr at 550°C. As shown in several experiments, this recycle-fluorination sequence would be effective in reducing residual plutonium to 0.009 w/o plutonium or 3% of the plutonium charge.

If the residual plutonium content of an alumina bed remained constant while several batches of fuel pellets were processed, the total plutonium losses in the waste alumina would be reduced to 1% or less of the plutonium charge. Consequently, a single 1200-g batch of alumina was used to process three batches of fuel pellets (720, 650, and 578 g) through the oxidation step, the fluorination step with 5-16 v/o fluorine at 350°C for uranium removal, and the recycle-fluorination step with 90 v/o fluorine for plutonium removal. The alumina bed was sampled during each experiment, and the pellet charge was determined by maintaining the pellet-to-alumina ratio at 0.6 for each run. The recommended recycle-fluorination sequence of 3 hr at 350°C, 6 hr at 350-550°C, and 1 hr at 550°C was used for each batch of pellets. In the final experiment, 4 hr at 550°C was used, giving a total recycle-fluorination period of 33 hr for the three batches of fuel pellets. The alumina bed from the final experiment contained 0.009 w/o uranium and 0.009 w/o plutonium, which corresponded to less than 0.01% of the uranium and 1% of the plutonium charged to the reactor. According to surface-area measurements and the conversion of alumina

to aluminum fluoride, the alumina bed was not significantly changed either physically or chemically during the reuse experiments. Therefore, an alumina bed can probably be used to process several batches of irradiated fuel pellets, thus reducing the total plutonium losses in the waste alumina from the fluid-bed fluoride-volatility process.

VI. CONCLUSIONS

The separation of uranium and plutonium from simulated, spent, power-reactor fuel pellets by fluid-bed fluoride-volatility methods has been demonstrated and carried out on a routine basis in a 2-in.-diam fluid-bed reactor system. When the pellets were pulverized to fine particles by oxidation, most of the uranium could be fluorinated to hexafluoride product at satisfactory production rates and fluorine utilization with 5-16 v/o fluorine at 350°C. The fluorination of uranium in the fluid bed followed a diminishing-sphere reaction mechanism which correlated closely with similar thermo-balance data. Thus, a method for scaleup of laboratory data to larger units is available.

During subsequent recycle-fluorination with 90 v/o fluorine, most of the plutonium was collected on sodium fluoride pellets which could be sampled efficiently to yield average plutonium material balances of 97%. About 5% of the plutonium charge remaining in the reactor was associated with fine particles on the walls and filters. This plutonium was recoverable and is considered a process inventory rather than a process loss. The plutonium contained in the alumina bed, which is considered a process loss, was reduced to about 3% of the plutonium charge by using a recycle-fluorination sequence consisting of 3 hr at 350°C, 6 hr at 350-550°C, and 1 hr at 550°C. The total plutonium loss was reduced to about 1% of the charge by reusing an alumina bed to process three batches of fuel pellets. This loss also is acceptable, and since the alumina bed was not significantly changed physically or chemically, the alumina beds can probably be used to process several batches of fuel pellets to effectively reduce total plutonium losses in the waste alumina from the fluid-bed fluoride-volatility process.

APPENDIX A

Summary of Average Operating ConditionsTABLE A.I. Average Operating Conditions for Experiments Using UO₂ Pellets

<u>Equipment:</u>	2-in.-diam fluid-bed reactor		
<u>UO₂ Pellets</u>			
Size:	0.5-in.-diam by 0.5-in. right cylinders		
Weight:	~655 g		
Bed Depth:	2 in.		
<u>Alumina Bed</u>			
Material:	Alcoa T-61 Tabular Alumina, nominal 48-100 mesh ^a		
Weight:	1100 g		
Depth:	12 in.		
<u>Bed Support:</u>	0.25-in.-diam nickel balls		
<u>Reactant Gas Diluent:</u>	Nitrogen		
Run:	A	B	C
<u>Two-zone Oxidation-Fluorination</u>			
Cumulative process time, hr	0-3.0	0-3.0	0-3.0
Reactor pressure, mm Hg	1340	1500	1480
Superficial gas velocity, ^b ft/sec	0.8	0.7	0.8
Oxygen concentration to pellet bed, v/o	18	11	10
Fluorine concentration to fluid bed, v/o	7	15	10
Temperature, °C	500	450	450
<u>Single-zone Fluorination</u>			
Cumulative process time, hr	-	-	3.0-4.0
Reactor pressure, mm Hg	-	-	1340
Superficial gas velocity, ^b ft/sec	-	-	0.7
Fluorine concentration to fluid bed, v/o	-	-	8
Temperature, °C	-	-	450
<u>Recycle-Fluorination</u>			
Cumulative process time, hr	3.0-18.0	3.0-23.0	4.0-23.5
Reactor pressure, mm Hg	1170	1340	1380
Superficial gas velocity, ^b ft/sec	0.6	0.6	1.1
Fluorine concentration to fluid bed, v/o	80-95	80-95	90
Cumulative process time at indicated temperature, hr			
450°C	-	3.0-8.0	4.0-8.5
500°C	3.0-8.0	8.0-13.0	8.5-13.5
550°C	8.0-18.0	-	13.5-23.5

^aThe -170 mesh fraction was screened from the alumina for Run C. This fraction represents 2% of the nominal 48-100 mesh material.

^bBased on cross-sectional area of reactor and calculated for operating temperature and pressure.

TABLE A.II. Average Operating Conditions for Runs 1-16

Run No.:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Equipment: 2-in.-diam fluid-bed reactor																
UO ₂ -PuO ₂ -F.P. Pellets: ^a Runs 1-6: Type I pellets, 0.5-in.-diam x 0.5-in. right cylinders																
Runs 7-16: Type II pellets, 0.5-in.-diam x 0.4-in. right cylinders																
Alumina Bed: ^a Run 3: Norton R.R. Alundum -40 +170 mesh																
Remaining runs: Alcoa T-61 Tabular Alumina, nominal 48 to 100 mesh (-170 mesh material was removed)																
Bed Support: 0.25-in.-diam nickel balls																
Reactant Gas Diluent: Nitrogen																
Material Charged to Reactor																
Weight of UO ₂ -PuO ₂ -F.P. pellets, g	654.6	653.7	653.1	654.5	650.3	653.2	652.1	645.9	647.1	635.7	332.9	651.6	1317.2	654.3	718.1	661.1
Pellet-bed depth, in.	2	2	2	2	2	2	2	2	2	2	1	2	4	2	2	2
Weight of alumina, g	1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	1100	1200	1100
Alumina-bed depth, in.	12	12	12	12	12	12	12	12	12	12	12	12	12	12	13	12
Weight of cesium fluoride, g	-	-	-	-	-	-	0.6	0.6	0.6	-	0.3	-	1.2	-	0.6	0.6
Two-zone Oxidation-Fluorination																
Cumulative process time, hr	0-4.0	0-3.0	0-3.0	0-3.0	0-3.0	0-3.0	0-3.0	0-3.0	0-3.0	0-3.0	0-1.5	0-3.0	0-5.0	0-3.0	0-3.0	0-3.0
Reactor pressure, mm Hg	1520	1500	1530	1510	1300	1540	1560	1540	1580	1420	1400	1480	1480	1440	1480	1500
Superficial gas velocity, ^b ft/sec	0.8	0.8	0.7	0.7	0.8	0.7	0.7	0.7	0.8	0.7	0.7	0.7	0.6	0.7	0.7	0.7
Oxygen concentration to pellet bed, v/o	11-19	20	16	32	19	18	20	20	18	20	20	21	0-20	20	21	21
Fluorine concentration to fluid bed, v/o	11	10	8	10	8	8	8	8	8	10	10	8	8	10	10	8
Temperature, °C	450-500	450	450	450	450	450	450	450	450	450	450	450	450	450	450	450
Single-zone Fluorination																
Cumulative process time, hr	4.0-5.0	3.0-4.0	3.0-4.0	-	3.0-4.0	3.0-5.0	3.0-4.5	3.0-5.0	3.0-4.0	3.0-4.0	1.5-2.0	3.0-4.0	5.0-6.0	3.0-4.0	-	-
Reactor pressure, mm Hg	1290	1400	1410	-	1080	1500	1400	1500	1490	1370	1340	1340	1410	1240	-	-
Superficial gas velocity, ^b ft/sec	0.7	0.6	0.6	-	0.8	0.6	0.6	0.7	0.6	0.7	0.6	0.7	0.7	0.7	-	-
Fluorine concentration to fluid bed, v/o	10	10	10	-	3	6	9	7	8	12	12	10	10	10	-	-
Temperature, °C	500	450	450	-	450	450	450	450	450	450	450	450	450	450	-	-
Recycle-Fluorination																
Cumulative process time, hr	5.0-20.0	4.0-24.0	4.0-24.0	3.0-23.0	4.0-17.0	5.0-17.0	4.5-13.0	5.0-17.0	4.0-24.0	4.0-17.0	2.0-14.0	4.0-16.0	6.0-18.0	4.0-16.0	3.0-11.0	3.0-11.0
Reactor pressure, mm Hg	1430	1430	1440	1470	1360	1340	1400	1370	1380	1370	1360	1360	1390	1330	1380	1360
Superficial gas velocity, ^b ft/sec	0.4	0.6	0.6	0.7	0.8	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.4	0.3	0.7
Fluorine concentration to fluid bed, v/o	80-95	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
Cumulative process time at indicated temperature, hr																
450°C	-	4.0-9.0	4.0-9.0	3.0-8.0	4.0-6.0	5.0-6.0	4.5-5.5	5.0-6.0	4.0-9.0	4.0-5.0	2.0-3.0	4.0-5.0	6.0-7.0	4.0-5.0	3.0-4.0	3.0-4.0
500°C	5.0-10.0	9.0-14.0	9.0-14.0	8.0-13.0	6.0-9.0	6.0-9.0	5.5-6.0 ^c	6.0-9.0	9.0-14.0	5.0-9.0	3.0-6.0	5.0-8.0	7.0-10.0	5.0-8.0	4.0-7.0 ^c	4.0-10.0 ^c
550°C	10.0-20.0	14.0-24.0	14.0-24.0	13.0-23.0	9.0-17.0	9.0-17.0	6.0-13.0	9.0-17.0	14.0-24.0	9.0-17.0	6.0-14.0	8.0-16.0	10.0-18.0	8.0-16.0	7.0-11.0	10.0-11.0

^aSee Section III.A for a description of these materials.^bBased on the cross-sectional area of the reactor and calculated for operating temperature and pressure.^cTemperature was increased from 450 to 550°C.

TABLE A.III: Average Operating Conditions for Runs 17-22

Equipment:	2-in.-diam fluid bed reactor					
UO ₂ -PuO ₂ -F.P. Pellets: ^a	Type II pellets, 0.5-in.-diam x 0.4-in. right cylinders					
Pellet-bed Depth:	2 in.					
Alumina Bed: ^a	Alcoa T-61 Tabular Alumina, nominal 48 to 100 mesh (-170 mesh material was removed)					
Alumina-bed Depth:	12 in.					
Bed Support:	0.25-in.-diam nickel balls					
Reactant Gas Diluent:	Nitrogen					
Run No.:	17	18	19	20	21	22
<u>Material Charged to Reactor</u>						
Weight of UO ₂ -PuO ₂ -F.P. pellets, g	654.6	651.9	720.5	649.7	577.7	650.4
Weight of alumina, g	1100	1100	1200	1115 ^b	970 ^c	1100
Weight of cesium fluoride, g	0.6	0.6	0.6	0.6	0.5	0.6
<u>Oxidation</u>						
Cumulative process time, hr	0-4.0	0-4.0	0-4.0	0-4.0	0-4.0	0-4.0
Reactor pressure, mm Hg	960	980	1040	980	1010	1040
Superficial gas velocity, ^d ft/sec	0.8	0.7	0.8	0.8	0.8	0.7
Oxygen concentration to pellet bed, v/o	19	20	20	20	20	20
Temperature, °C	450	450	450	450	450	450
<u>Fluorination (Once-through Flow)</u>						
Cumulative process time, hr	4.0-9.5	4.0-6.0	4.0-6.0	4.0-6.0	4.0-6.0	4.0-6.0
Reactor pressure, mm Hg	1470	1500	1440	1340	1350	1490
Superficial gas velocity, ^d ft/sec	0.6	0.6	0.7	0.6	0.6	0.6
Fluorine concentration to fluid bed, ^e v/o	10	16	15	6-15	5-15	5-16
Temperature, hr						
300°C	4.0-6.5	350	350	350	350	350
350°C	6.5-9.5					
<u>Recycle-Fluorination</u>						
Cumulative process time, hr	9.5-21.5	6.0-16.0	6.0-16.0	6.0-16.0	6.0-19.0	6.0-21.0
Reactor pressure, mm Hg	1430	1380	1260	1350	1360	1420
Superficial gas velocity, ^d ft/sec	0.8	0.8	0.7	0.6	0.6	0.6
Fluorine concentration to fluid bed, v/o	90	90	90	90	90	90
Cumulative process time at indicated temperature, hr						
350°C	9.5-12.5	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
350-550°C ^f	12.5-18.5	9.0-15.0	9.0-15.0	9.0-15.0	9.0-15.0	g
550°C	18.5-21.5	15.0-16.0	15.0-16.0	15.0-16.0	15.0-19.0	19.0-21.0

^aSee Section III.A for a description of these materials.

^bResidual bed from Run 19.

^cResidual bed from Run 20.

^dBased on the cross-sectional area of the reactor and calculated for operating temperature and pressure.

^eFluorine was introduced through a side inlet (located 6 in. above the bed support of nickel balls) for approximately the first half hour and subsequently fed to the bottom of the reactor.

^fReactor temperature increased 5°C/9 min.

^gThe temperature sequence for Run 22 included 3 hr at 375°C, 3 hr at 400°C, 2 hr at 450°C, and 2 hr at 500°C at cumulative process times of 9.0-19.0 hr.

APPENDIX B

Uranium and Plutonium Content of the Fluidized Alumina Bed during Runs 1-22

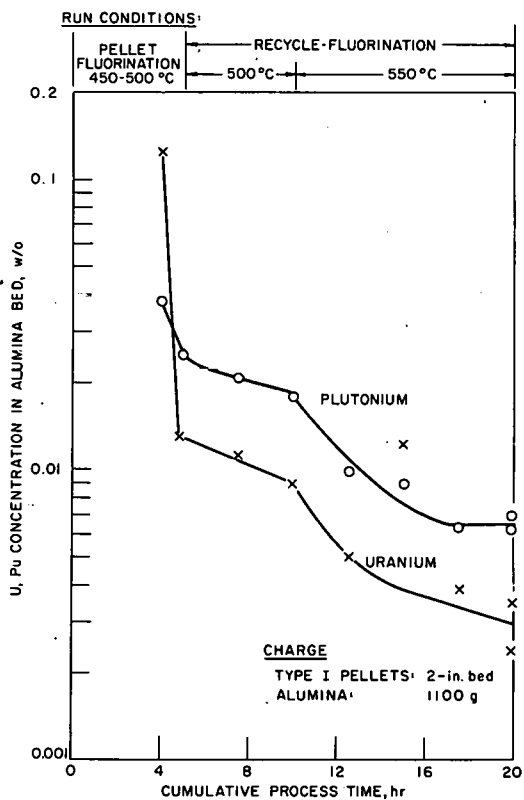


Fig. B.1
 Uranium and Plutonium Concentration
 in Fluidized Alumina Bed during Run 1

108-8908 Rev. 2

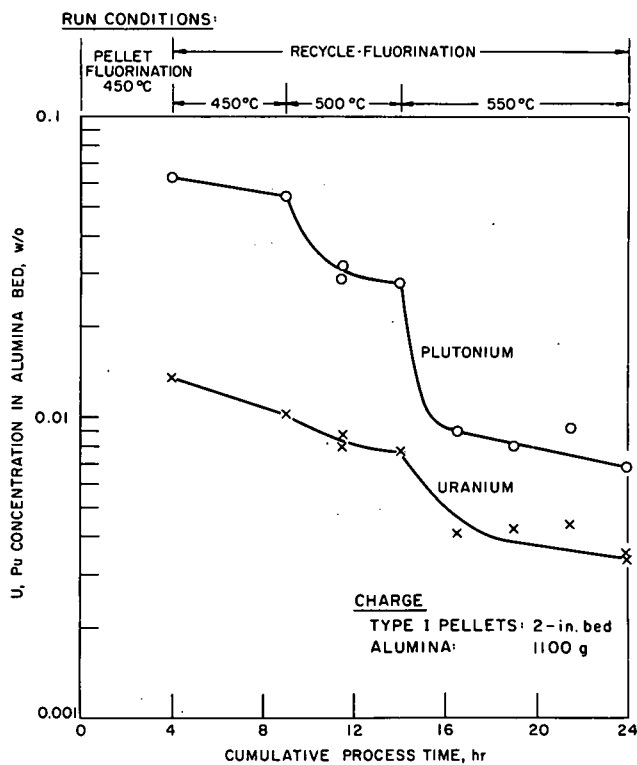


Fig. B.2
 Uranium and Plutonium Concentration
 in Fluidized Alumina Bed during Run 2

108-8915 Rev. 1

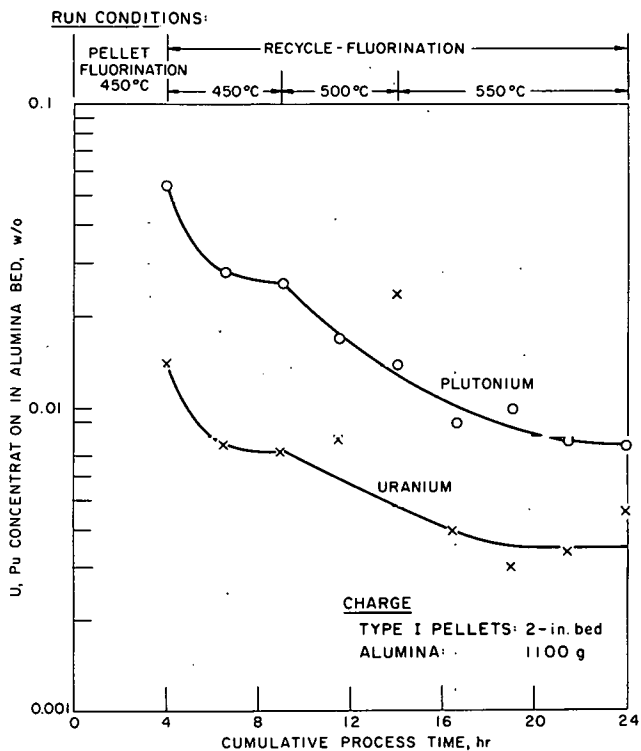


Fig. B.3
Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 3

108-8912

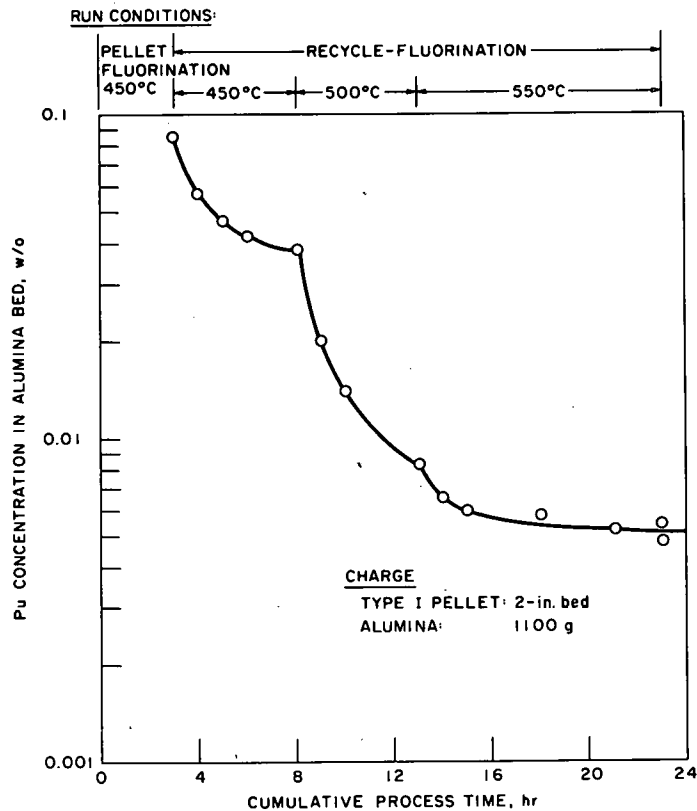
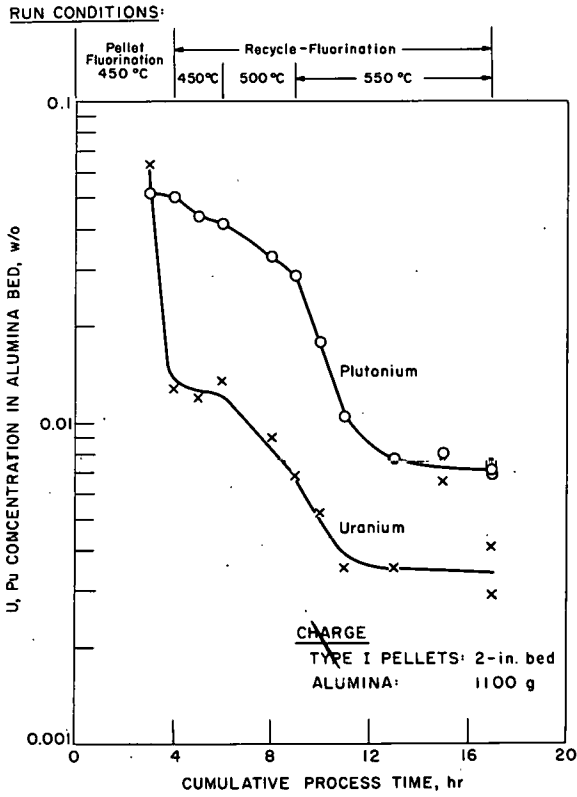
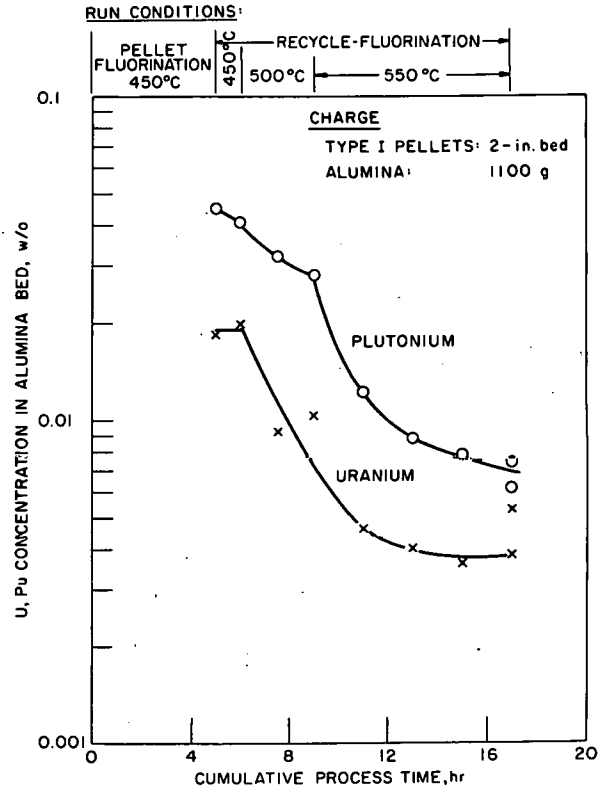


Fig. B.4
Plutonium Concentration in Fluidized Alumina Bed during Run 4



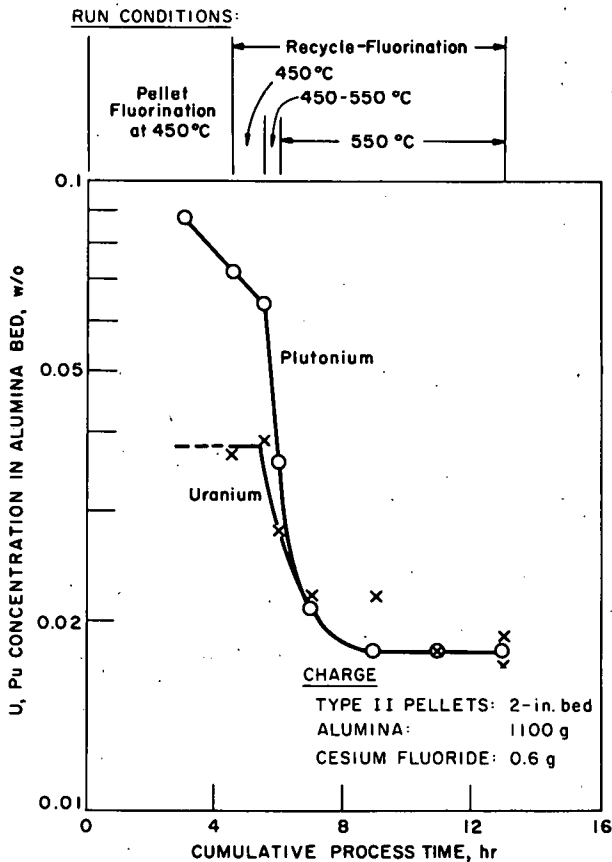
108-9286 Rev. 1

Fig. B.5. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 5



108-9128 Rev. 2

Fig. B.6. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 6



108-9291 Rev. 1

Fig. B.7
Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 7

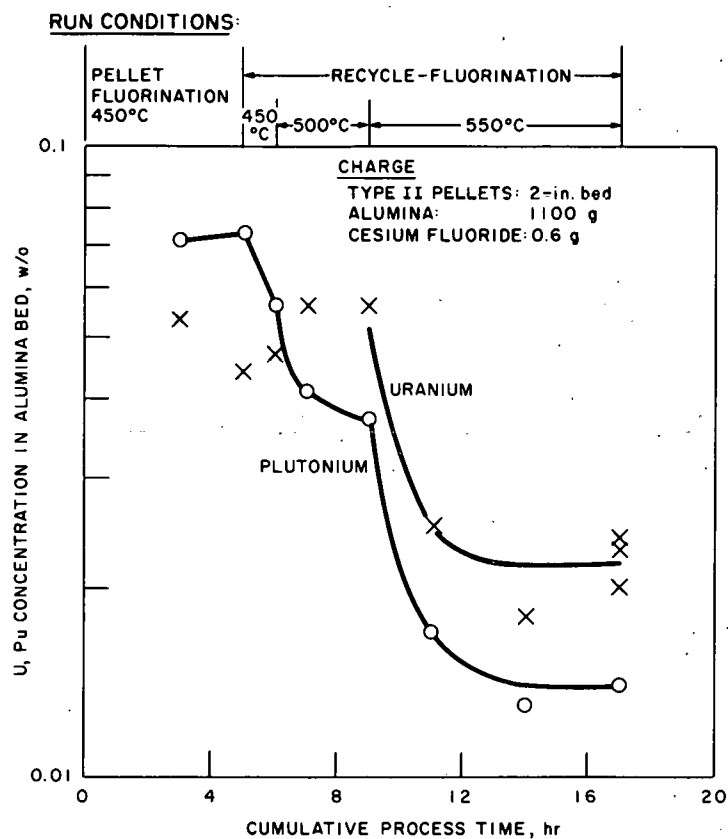
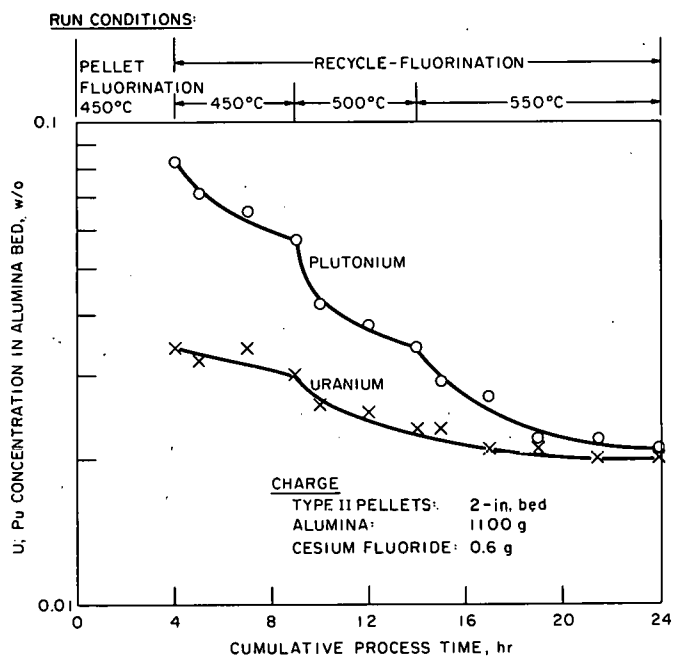


Fig. B.8

Uranium and Plutonium Concentration
in Fluidized Alumina Bed during Run 8

Fig. B.9
Uranium and Plutonium Concentration
in Fluidized Alumina Bed during Run 9



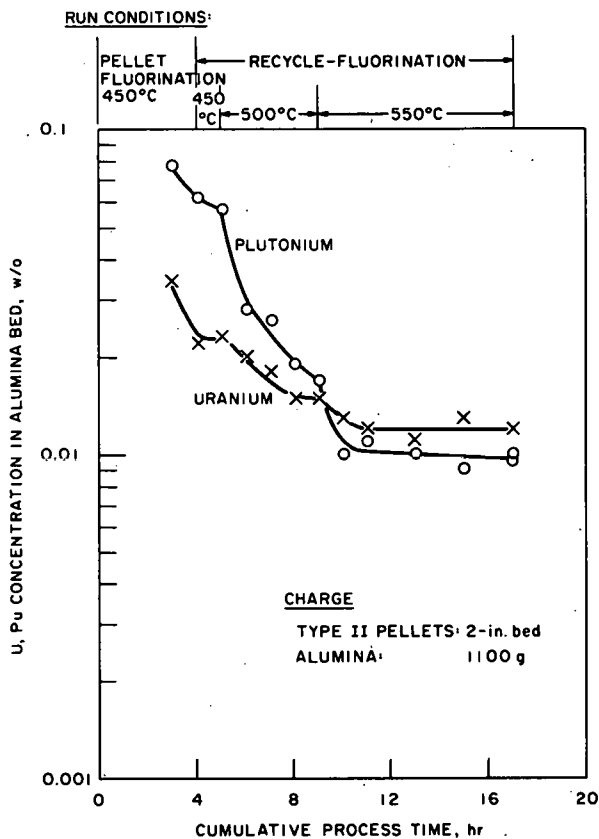


Fig. B.10

Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 10

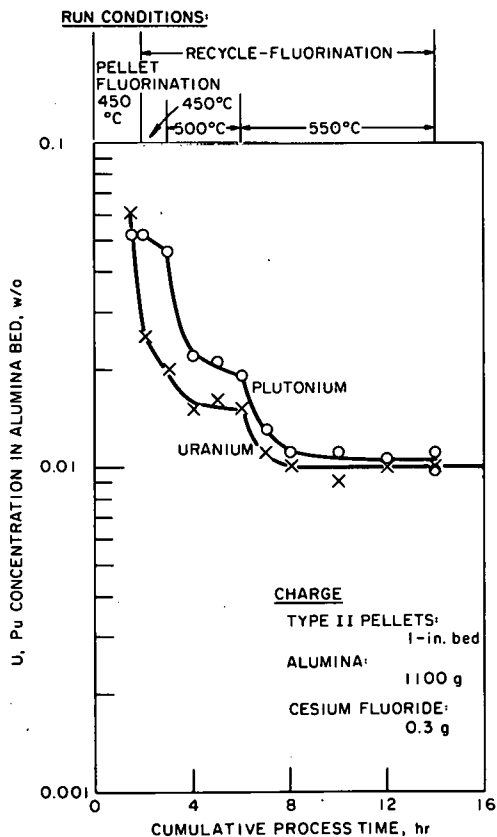


Fig. B.11

Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 11

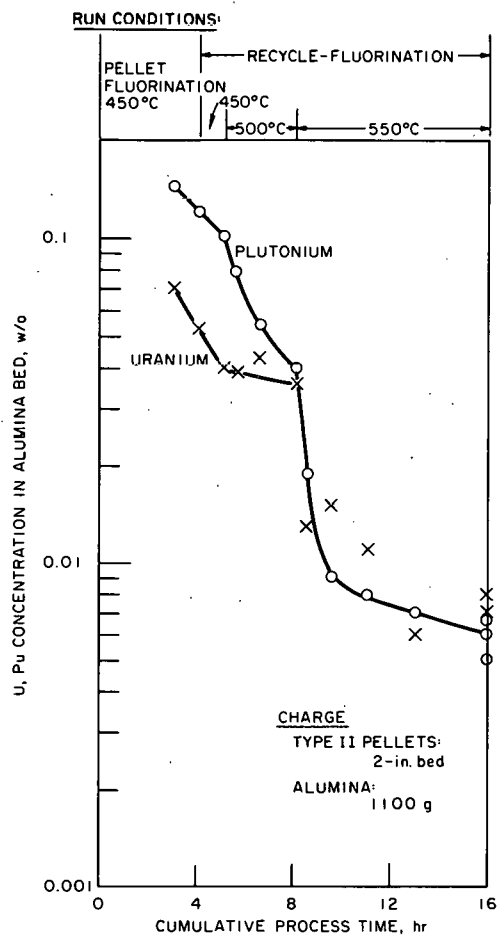


Fig. B.12

Uranium and Plutonium Concentration
in Fluidized Alumina Bed during Run 12

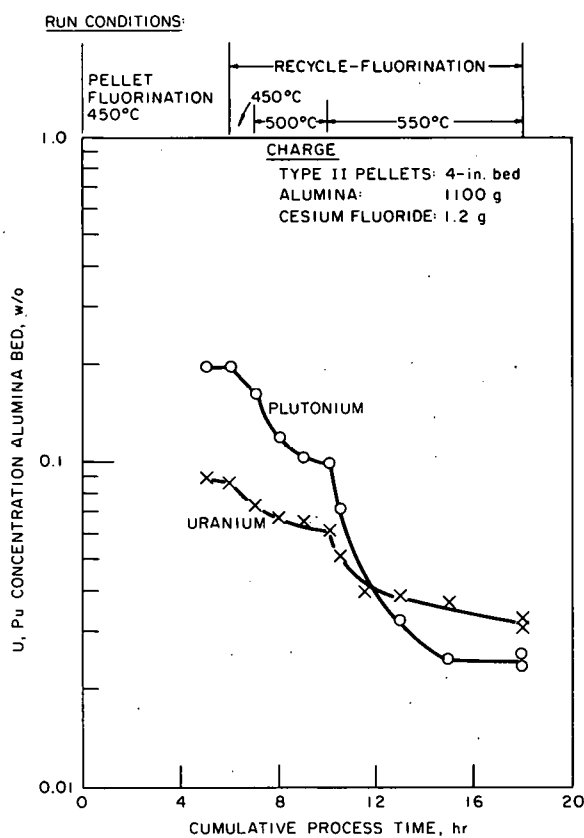


Fig. B.13

Uranium and Plutonium Concentration
in Fluidized Alumina Bed during Run 13

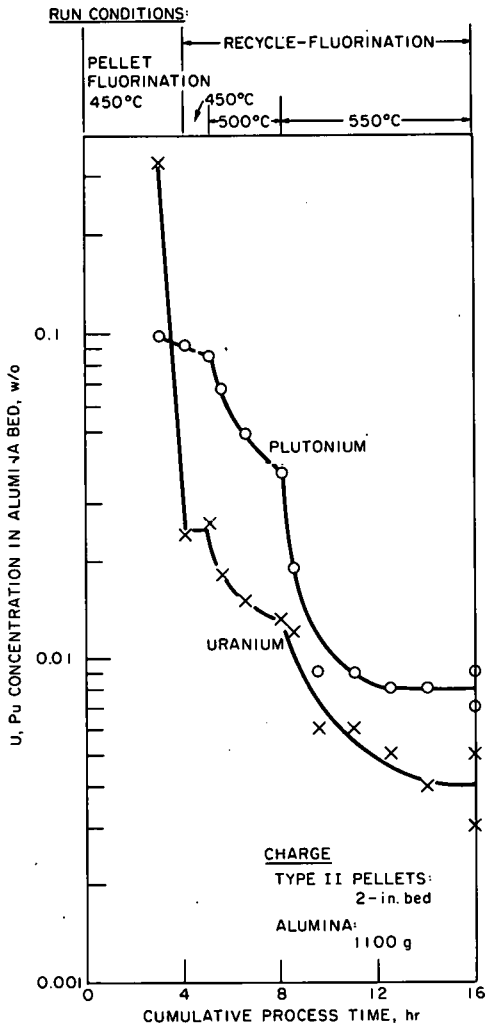


Fig. B.15
Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 15

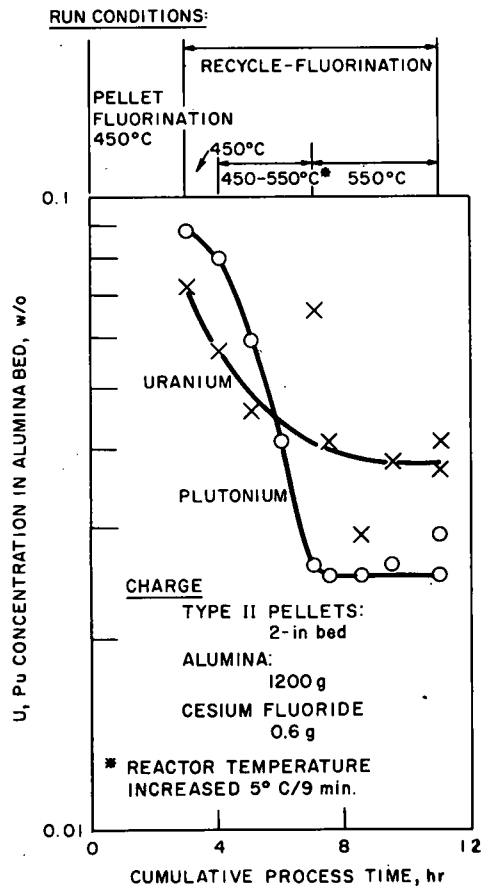


Fig. B.14
Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 14

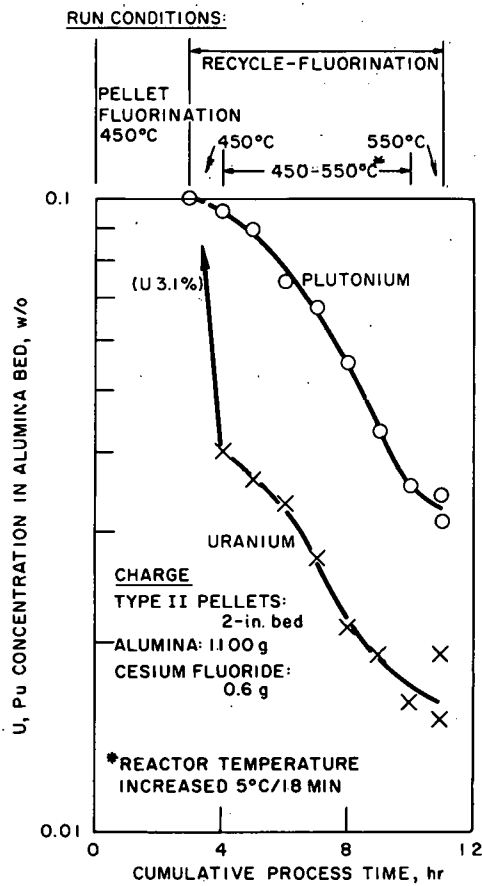
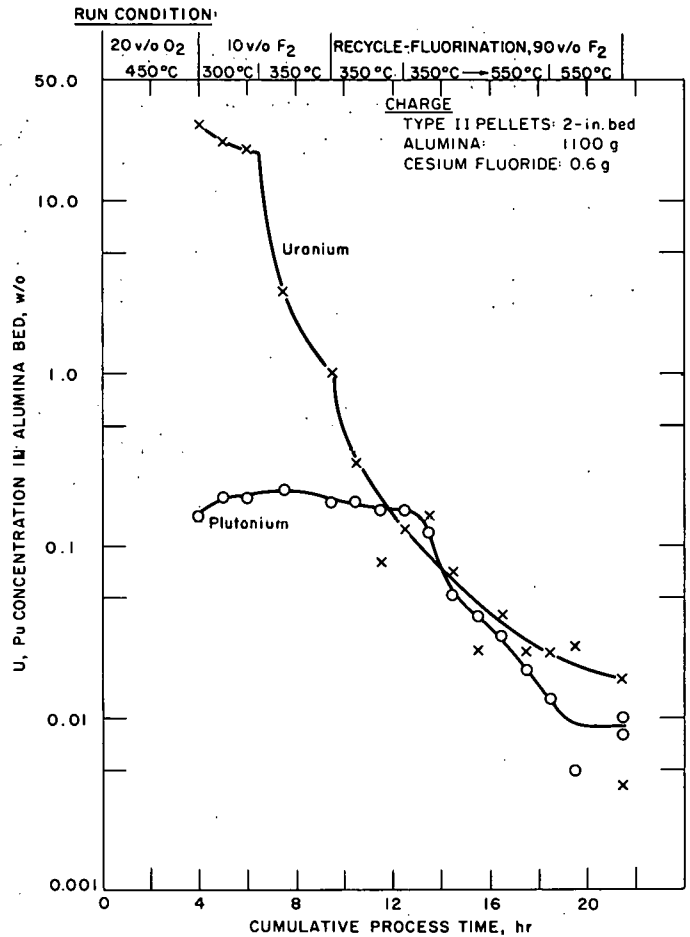


Fig. B.16. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 16



308-93 Rev. 1

Fig. B.17. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 17

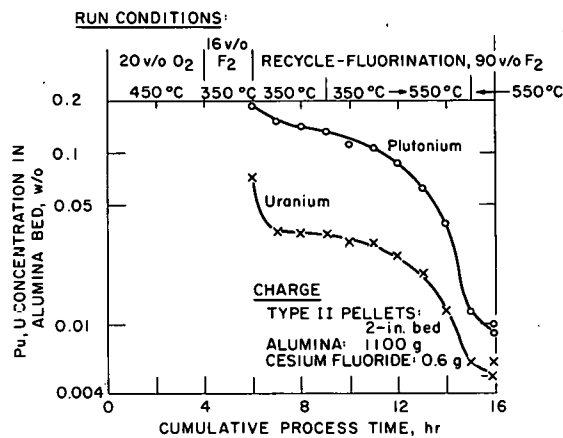
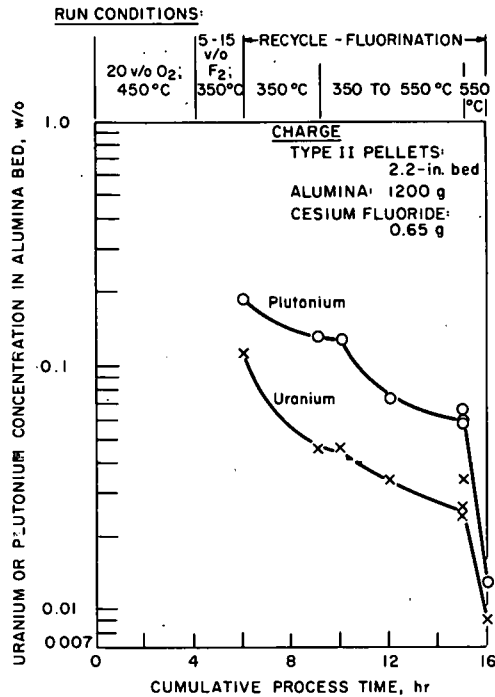


Fig. B.18

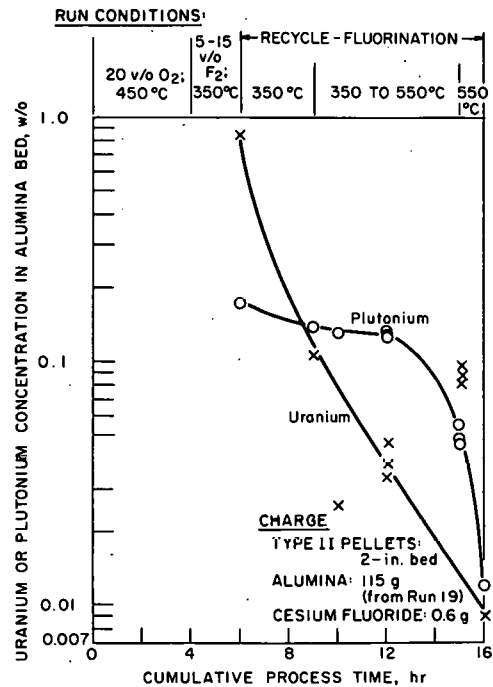
Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 18

308-58 Rev. 1



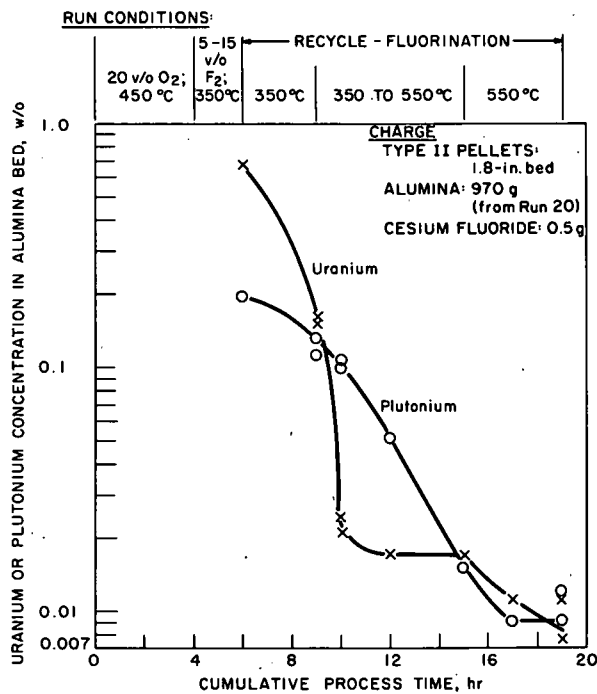
308-530A

Fig. B.19. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 19



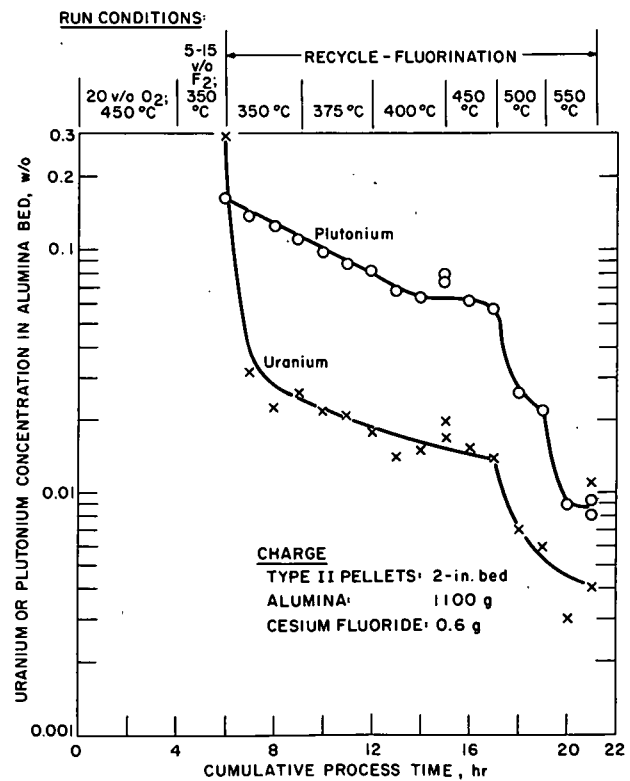
308-530B

Fig. B.20. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 20



308-530C

Fig. B.21. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 21



308-409 Rev. 1

Fig. B.22. Uranium and Plutonium Concentration in Fluidized Alumina Bed during Run 22

APPENDIX C

Computer Program for Process Data Reduction

A computer program, based on PACER-65,³¹ was written to calculate operating conditions from basic run data. The application of PACER-65, a generalized automatic flowsheet calculator, to process data reduction has been described by Koppel *et al.*³²

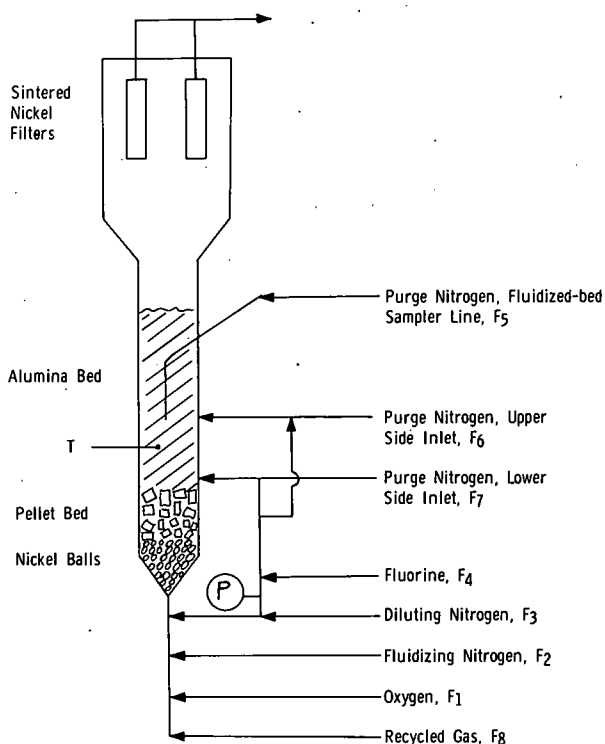


Fig. C.1. Variables Pertinent to Process Data Reduction

At regular intervals during an experiment, operating data for the reactor system were recorded; this information included system pressures, temperatures, and gas flow rates. Variables pertinent to the data reduction are listed below and shown in Fig. C.1. Gas flow rates were determined by the computer from calibration data for the rotameters and a sum-interpolation routine which gave the gas flow rate as a function of rotameter reading and system pressure. An exception to this routine was the gas flow, F_8 , which was directly obtained from a thermal flowmeter. The symbols and variables used in the calculations were as follows:

<u>Symbol</u>	<u>Variable</u>
F_1	Oxygen flow rate, liters/min
F_2	Fluidizing-nitrogen flow rate, liters/min
F_3	Diluting-nitrogen flow rate, liters/min
F_4	Fluorine flow rate, liters/min
F_5	Purge nitrogen, fluidized bed sampler line, liters/min
F_6	Purge nitrogen, upper side inlet, liters/min
F_7	Purge nitrogen, lower side inlet, liters/min
F_8	Recycled gas, liters/min
T	Fluidized alumina-bed temperature, °C
P	System pressure, mm Hg

The volumetric flow rates given in the above were calculated for the specified conditions of 21.1°C and 760 mm Hg. For each set of run data, operating conditions were calculated for the various processing steps as follows:

1. Two-zone Oxidation-Fluorination Runs

a. Oxidation and Fluorination

(1) Total gas to pellet bed = $F_1 + F_2$, liters/min.

(2) Oxygen concentration to pellet bed = $\frac{100F_1}{F_1 + F_2}$, v/o.

(3) Total gas to fluid bed = $\sum_1^7 F_n$, liters/min.

(4) Fluorine concentration to fluid bed = $\frac{100F_4}{\sum_1^7 F_n}$, v/o.

(5) Superficial velocity to pellet bed at operating conditions:

$$u = \frac{\text{gas flow at temperature and pressure}}{\text{empty column cross-sectional area}};$$

$$u_1 = (F_1 + F_2) \frac{1 \text{ min}}{60 \text{ sec}} \cdot \frac{1 \text{ ft}^3}{28.32 \text{ liter}} \cdot \frac{1}{0.0233 \text{ ft}^2} \cdot \frac{T + 273}{294.1^\circ\text{K}} \cdot \frac{760 \text{ mm Hg}}{P - 20};$$

$$u_1 = \frac{(F_1 + F_2)(T + 273)}{15.3(P - 20)}, \text{ ft/sec.}$$

(The factor $P - 20$ occurs because the reactor pressure is 20 mm Hg less than the system pressure.)

(6) Superficial velocity to fluid bed at operating conditions:

$$u = \frac{(T + 273) \sum_1^7 F_n}{15.3(P - 20)}.$$

b. Fluorination with Fluorine during Once-through Gas Flow

(1) Total gas to fluid bed = $\sum_2^7 F_n$, liters/min.

$$(2) \text{ Fluorine concentration to fluid bed} = \frac{100F_4}{\sum_2^7 F_n}, \text{ v/o.}$$

2. Two-step Oxidation and Fluorination Runs

a. Oxidation

$$(1) \text{ Total gas to pellet bed} = \sum_1^3 F_n, \text{ liters/min.}$$

$$(2) \text{ Oxygen concentration to pellet bed} = \frac{100F_1}{\sum_1^3 F_n}, \text{ v/o.}$$

$$(3) \text{ Total gas to fluid bed} = F_1 + F_2 + F_3 + F_5 + F_6 + F_7, \text{ liters/min.}$$

$$(4) \text{ Superficial gas velocity to pellet bed} = \frac{(T + 273) \sum_1^3 F_n}{15.3(P - 20)}, \text{ ft/sec.}$$

$$(5) \text{ Superficial gas velocity to fluid bed} =$$

$$\frac{(F_1 + F_2 + F_3 + F_5 + F_6 + F_7)(T + 273)}{15.3(P - 20)}, \text{ ft/sec}$$

b. Fluorination

Equations are given above for fluorination with fluorine, once-through flow.

3. Recycle-Fluorination for All Runs

$$(1) \text{ Total gas to fluid bed} = \sum_4^8 F_n, \text{ liters/min.}$$

$$(2) \text{ Superficial gas velocity to fluid bed} = \frac{(T + 273) \sum_4^8 F_n}{15.3(P - 20)}, \text{ ft/sec}$$

The calculated results are printed as shown in Table C.I. In addition to these results for each time interval for a given operation, a summary table is also generated listing the range of operating conditions for the complete run. Table C.II is a typical example of this output. Given in the summary table are the type, size, and weight of the fuel-pellet charge plus the

pellet-bed depth, pellet-bed support, and the fluid-bed material, including the size limits and static-bed height, as well as the cumulative process time for the various processing steps and the ranges of the corresponding operating variables.

TABLE C.I. Computer Output Data Sheet for Point-to-Point Calculations

OXIDATION WITH O₂

TIME	REACTOR PRESSURE	GAS TO FLUID BED	VELOCITY FLUID BED	TEMP.	GAS TO PELLET BED	O ₂ CONC. PELLET BED	VELOCITY PELLET BED
0.0	960	14.5	0.72	450	14.4	20	0.71
1.0	960	14.5	0.72	450	14.4	20	0.71
1.5	980	15.0	0.72	450	14.9	21	0.72
2.0	980	15.0	0.72	450	14.9	21	0.72
2.5	980	15.0	0.72	450	14.9	21	0.72
3.0	990	15.0	0.72	452	14.9	21	0.72
3.5	960	14.8	0.72	445	14.7	21	0.72

FLUORINATION WITH F₂-ONCE-THROUGH FLOW

TIME	REACTOR PRESSURE	GAS TO FLUID BED	VELOCITY FLUID BED	TEMP.	F ₂ CONC. FLUID BED
4.0	1480	22.9	0.63	346	17
4.5	1505	23.1	0.65	372	16
5.0	1530	23.2	0.62	352	16
5.5	1530	23.2	0.62	350	16
6.0	1530	23.2	0.61	346	16

FLUORINATION WITH F₂-RECYCLE

TIME	REACTOR PRESSURE	GAS TO FLUID BED	VELOCITY FLUID BED	TEMP.
6.1	1410	20.7	0.59	342
7.0	1410	23.7	0.69	355
8.0	1360	23.4	0.71	355
9.0	1390	24.1	0.70	350
10.0	1390	23.4	0.73	391
11.0	1410	23.4	0.75	418
12.0	1380	24.4	0.83	448
13.0	1405	23.4	0.82	480
14.0	1380	23.4	0.90	536
15.0	1380	23.4	0.91	545

TABLE C.II. Computer Output Data Sheet; Summary
of Operating Conditions

AVERAGE OPERATING CONDITIONS FOR RUN 18

EQUIPMENT 2-IN. DIA. FLUID-BED REACTOR

U02=PU02 (+F,P.) PELLETS

SIZE 0.48-IN. DIA. X 0.41-IN. RIGHT CYLINDERS
WEIGHT 651.9G
BED DEPTH 2-IN.
BED SUPPORT NICKEL BALLS
CSF ADDED 0.6 G

ALUMINA FLUID BED

MATERIAL ALCOA Y-61 ALUMINA
SIZE LIMITS NOMINAL 48-100 MESH (-170 MESH FRACTION REMOVED)
WEIGHT 1100G
STATIC BED DEPTH 12-IN.

OXIDATION WITH O₂

CUMULATIVE PROCESS TIME (HR.)	0.0-4.0
REACTOR PRESSURE (MM HG)	960- 990
TOTAL GAS FLOW TO FLUID BED (L/MIN)	14.5- 15.0
SUPERFICIAL VELOCITY (FT/SEC)	0.72- 0.72
OXYGEN CONCENTRATION TO PELLET BED (PERCENT)	20- 21
DILUENT	N ₂
TEMPERATURE	450C

FLUORINATION WITH F₂-ONCE-THROUGH FLOW

CUMULATIVE PROCESS TIME (HR.)	4.0-6.0
REACTOR PRESSURE (MM HG)	1480- 1530
TOTAL GAS FLOW TO FLUID BED (L/MIN)	22.9- 23.2
SUPERFICIAL VELOCITY (FT/SEC)	0.61- 0.65
FLUORINE CONCENTRATION TO FLUID BED (PERCENT)	16- 17
DILUENT	N ₂
TEMPERATURE	350C

FLUORINATION WITH F₂-RECYCLE

CUMULATIVE PROCESS TIME (HR.)	6.0 16.0
REACTOR PRESSURE (MM HG)	1360- 1410
TOTAL GAS FLOW TO FLUID BED (L/MIN)	20.7- 24.4
SUPERFICIAL VELOCITY (FT/SEC)	0.59- 0.91
FLUORINE CONCENTRATION TO FLUID BED (PERCENT)	90
DILUENT	N ₂
TEMPERATURE	350C, 6.0-9.0 HR 350-550C, 9.0-15.0 HR 550C, 15.0-16.0 HR

ACKNOWLEDGMENTS

We acknowledge the continued interest and support of these studies given by R. C. Vogel and A. A. Jonke. The suggestions and programming help given by Professor Lowell B. Koppel were instrumental in setting up the computer programs used for data reduction and analysis. The programs were reduced to practice with the assistance and liaison efforts of John B. Anderson of the Applied Mathematics Division. The many sample analyses demanded of the Chemical Engineering Division Analytical Group, under the direction of R. P. Larsen and L. E. Ross, were carried out by E. C. Kucera, R. V. Schablaske, and their co-workers.

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