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Argonne National Laboratory

ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 10. Bench-scale Studies on Irradiated,
Highly Enriched, Uranium-alloy Fuels

by

A. A. Chilenskas, K. S. Turner,
J. E. Kincinas, and G. L. Potts

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	7
I. INTRODUCTION	8
II. EQUIPMENT AND PROCEDURE	10
A. The Processing Unit	10
B. Instrumentation	12
C. The Cave Facility and Remote Operations.	13
1. The Cave Facility	13
2. Remote Operations.	16
D. The Model 3 Electric Master-Slave Manipulators.	20
E. Sampling and Analysis.	20
1. Irradiated Charges.	20
a. Uranium-Zircaloy.	20
b. Uranium-Alumium.	20
2. Process Sampling	21
a. Reactor and Filter Beds	21
b. Sodium Fluoride Beds	21
c. Activated-alumina Beds	21
3. Analytical Methods.	21
F. Waste Disposal	22
III. RESULTS AND DISCUSSION	24
A. Experiments with Nonirradiated Fuel Materials.	24
B. Experiments with Irradiated Fuel Materials.	25
1. Recovery of Uranium	25
2. Uranium Decontamination Factors	26
3. Distribution of Fission Products and Neptunium	31
a. Distribution following Hydrochlorination Step	35
b. Distribution following Fluorination Step	36
4. Use of MgF_2 for Removal of Technetium and Neptunium	38
5. Gamma Composition of Process Streams	38
6. Fission-product Balances	39
IV. SUMMARY AND CONCLUSIONS.	41
ACKNOWLEDGMENTS	42
REFERENCES	43

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Schematic Flowsheet for Processing Uranium-alloy Fuels . .	8
2.	Fluid-bed Fluoride Volatility Processing Unit Used for Bench-scale Studies on Irradiated Fuels	10
3.	Schematic Flowsheet of FBV Processing Unit Used for Bench-scale Studies on Irradiated Fuels	11
4.	Chemical Engineering Senior Cave Facility	14
5.	Process Unit before Installation in Senior Cave	15
6.	Fluid-bed Reactor Discharge Valve	16
7.	Reactor and Packed-bed Filter, Top View	17
8.	Impact Wrench Sealing the Condenser	17
9.	Removal of Cartridge from Sodium Fluoride Trap.	18
10.	Cartridge-dumping Tool	19
11.	Transfer of Reactor-bed Sample to a Motorized Mortar Grinder	19
12.	Distribution of Uranium and Fission Products following FBV Processing of Irradiated 5-yr-cooled Uranium- Zircaloy Alloy--Runs SCAZ-1 and -2	27
13.	Distribution of Uranium and Fission Products following FBV Processing of Irradiated 7-month-cooled Uranium- Aluminum Alloy--Run SCAA-1.	28
14.	Distribution of Uranium and Fission Products following FBV Processing of Irradiated 7-month-cooled Uranium- Aluminum Alloy--Run SCAA-2.	29
15.	Distribution of Uranium and Fission Products following FBV Processing of Irradiated 3-month-cooled Uranium- Aluminum Alloy--Runs SCAA-3 and -4	30

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Equipment Size and Loading Specifications.	12
II.	Conditions during FBV Processing of Nonirradiated Uranium-alloy Fuels	24
III.	Uranium Distribution following FBV Processing of Non-irradiated Uranium-alloy Fuels	25
IV.	Comparison of Uranium Removals from Reactor and Filter Beds for Nonirradiated and Irradiated Charges.	25
V.	Uranium Decontamination Factors Obtained by FBV Processing of Irradiated Uranium-alloy Fuels	26
VI.	Summary of Analyses for Irradiated Uranium-Zircaloy--Run SCAZ-1.	32
VII.	Summary of Analyses for Irradiated Uranium-Zircaloy--Run SCAZ-2.	32
VIII.	Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-1.	33
IX.	Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-2.	33
X.	Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-3.	34
XI.	Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-4.	34
XII.	Fission Products Volatilized and Collected Downstream of Packed-bed Filter.	34
XIII.	Composition of Charge and Process Streams in Terms of Their Gamma-active Fission Products--Runs SCAZ-1 and -2.	35
XIV.	Composition of Charge and Process Streams in Terms of Their Gamma-active Fission Products--Runs SCAA-1 and -2.	35

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ABSTRACT

A series of six experiments using irradiated uranium-Zircaloy and uranium-aluminum alloy fuels using fluid-bed fluoride volatility (FBV) processing techniques has been completed. These experiments were performed to determine the distribution of uranium and fission products following the various process steps and to indicate what decontamination factors can be realized. A hydrochlorination step was employed to remove the zirconium or aluminum from the uranium in the fluid-bed reactor. A fluorination step was employed (using fluorine) to volatilize the uranium as UF_6 . A packed bed of granular alumina downstream of the fluid-bed reactor removed particulate matter entrained in the process gas, and beds of NaF pellets were used for additional decontamination.

The retention of uranium in the reactor bed and the filter bed following the processing of irradiated uranium-Zircaloy or uranium-aluminum alloy was less than 1%, which is acceptable and comparable to that found in processing nonirradiated uranium alloys.

Decontamination factors for the activities Ce, Sr, Cs, Ru, Sb, Zr, and Nb from uranium ranged from 3.5×10^5 to 1×10^8 for the final two experiments. The decontamination from gamma activity for these two runs was high and such that the principal gamma activity found with the product was due to ^{237}U . The decontamination factor for tellurium was 5.9×10^4 ; the factors for Mo, Tc, and Np were 44.6, 2.9, and 3.5, respectively.

The distribution of fission products following hydrochlorination showed the principal volatile fission products to be Zr, Nb, Kr, and I. The activities that are only partially volatile (<10%) are Sb, Te, Mo, and Tc. The activities that are nonvolatile are Ce, Cs, Sr, and Ru.

The distribution of the fission products following fluorination showed the highly volatile fission products to be Sb, Mo, Tc, Np, Nb, and Te. A small amount of zirconium was transported, probably by volatilization, from the reactor. The activities Ce, Cs, Sr, and Ru were essentially nonvolatile.

Iodine volatilized essentially completely during the hydrochlorination step. A caustic scrubber was successful in removing iodine from the process off-gas.

Krypton volatilized completely during the hydrochlorination step. It was released under controlled conditions to the atmosphere.

Tellurium was completely removed from the process off-gas during fluorination by the use of an activated alumina trap.

I. INTRODUCTION

Although irradiated fuels have been reprocessed for many years by solvent extraction processes, other reprocessing methods, which do not depend on organic solvents and aqueous media, appear to have important economic advantages. One such reprocessing method depends upon conversion of fuel materials to volatile compounds, such as uranium hexafluoride and plutonium hexafluoride; fractional distillation and/or adsorption techniques are employed to accomplish the necessary high degree of separation from fission products and other constituents of the spent fuel.¹

Processes based on volatilization methods are under development for application to a variety of nuclear fuels of both the low-enrichment and high-enrichment type. Previous publications in this series have detailed the results of bench-scale (1½-in. reactor) investigations with nonirradiated zirconium-uranium,² nonirradiated aluminum-uranium, and nonirradiated stainless steel-cermet fuels.³ A pilot-plant study with a 6-in. reactor utilizing nonirradiated Zircaloy-uranium and aluminum-uranium alloy fuels has also been completed and reported.⁴

108-8271 Rev. 3

Fig. 1. Schematic Flowsheet for Processing Uranium-alloy Fuels

A schematic flowsheet of a fluid-bed fluoride volatility process for enriched uranium alloy fuels is shown in Fig. 1. The conceptual operation of the process consists of two main chemical-reaction steps conducted in a single vessel (halogenation reactor). The first is a separation step, hydrochlorination, in which the alloying materials are volatilized; the second is a recovery step, fluorination, in which the

uranium is volatilized and recovered as the hexafluoride. The reactions are conducted while the fuel is immersed in a bed of inert alumina granules fluidized by nitrogen and reagent gases.

In the first step, the alloying elements of the fuel are converted by reaction with HCl into chlorides that are volatile at the reaction temperature. The volatile chlorides of the alloying metal, mainly $ZrCl_4$ for zirconium alloys, and $AlCl_3$ for aluminum alloys, are carried out of the system and are reacted with steam in a second fluid-bed reactor (pyrohydrolysis reactor) to give a solid oxide waste. In the conceptual flowsheet, the HCl regenerated during the pyrohydrolysis operation may be recycled. The uranium forms particulate chlorides, which are relatively nonvolatile and remain in the halogenation reactor system. Any particulate uranium chlorides entrained from the fluid bed by the exiting gas stream are filtered by down-flow of the gas through a static bed of particulate alumina. This type of filter is used for high-temperature operation because of its simplicity and its suitability with respect to corrosion problems.

In the recovery step, the uranium chlorides in both the halogenation reactor fluid bed and the packed-bed filter are reacted with anhydrous hydrogen fluoride and then gaseous fluorine, and the product (UF_6) is recovered by sorption on beds of NaF or in cold traps maintained at about $-80^\circ C$. The excess hydrogen fluoride and fluorine may be disposed of or may be recycled to the halogenation reactor. The UF_6 may be further decontaminated by distillation or by selective sorption on NaF. The decontaminated UF_6 is then returned for isotope separation and reconversion to the metal or oxide for fuel refabrication.

Most of the fission-product radioactivity will be distributed between the particulate alumina in the reactor and packed-bed filter, and the solid oxides produced in the pyrohydrolysis reactor. Low-level solid wastes such as NaF pellets may be produced in the UF_6 decontamination steps. Scrub solutions can be vaporized to supply steam to the pyrohydrolysis reactor so that no aqueous wastes need be treated.

The work described in this report was performed with a $1\frac{1}{2}$ -in. reactor similar to that used in the previous bench-scale work but located in a shielded cave to permit a study using irradiated fuels. The objectives of this study were (1) to establish if fission products or the presence of a radiation field has a significant effect upon uranium recovery from uranium-alloy fuels, (2) to determine what uranium decontamination factors were possible, and (3) to determine the uranium and fission-product distribution following each process step.

II. EQUIPMENT AND PROCEDURE

A. The Processing Unit

A photograph of the equipment before its installation in the shielded facility is shown in Fig. 2. A schematic flowsheet for the apparatus is shown in Fig. 3. The hydrochlorination step is performed with valve V1 closed and valve V2 open. The HCl/N_2 gas mixture flows from the packed-bed filter to the condenser,* through the disposable filter to the scrubber, and then to the atmosphere through the cave stack. The ZrCl_4 (or AlCl_3) generated in the reactor is removed from the gas stream by the condenser (cooled by natural convection). Experience with the unirradiated fuels showed that a filter is required after the condenser to remove chloride fines, which cause plugging of the line to the scrubber. The filter consists of a small section of pipe, packed with glass wool, which can be removed and replaced remotely for each run. Excess HCl is scrubbed from the nitrogen-gas stream by continuously recirculated H_2O , NaOH , or KOH solution in a scrub tower. A demister removes entrained scrub solution from the gas stream before discharge of the gas to the cave exhaust duct.

Fig. 2

Fluid-bed Fluoride Volatility
Processing Unit Used for
Bench-scale Studies on
Irradiated Fuels

108-7239

*In the conceptual process flowsheet, the ZrCl_4 or AlCl_3 is removed from the gas stream by a fluid-bed pyrohydrolyzer as noted in Section I. A condenser was used in the work with irradiated fuels to reduce the complexity of the apparatus needed in the hot cell.

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Fig. 3. Schematic Flowsheet of FBV Processing Unit
Used for Bench-scale Studies on Irradiated Fuels

When the hydrochlorination step has been completed, the high-temperature valves are reversed (V1 opened, V2 closed) and the fluorination step begun. In the experimental work with irradiated fuels, the HF step as described previously for the general flowsheet was not employed. The HF step is desirable for a flowsheet in which the UF_6 product leaving the reactor is cold-trapped before purification. For the experiments with irradiated fuel, UF_6 sorption on NaF before cold-trapping obviated the

need for the HF step. During the fluorination step, UF_6 is generated in the fluid-bed reactor, passes through traps NaF-1 and NaF-2 (maintained at 400°C for removal of certain fission products), and is collected on trap NaF-3, which is maintained at $100\text{--}150^\circ\text{C}$. A fourth NaF trap (at room temperature) serves as a backup for the NaF-3 trap. The gas flow continues to a fluorine absorption tower containing 1/4-in.-diam activated alumina balls and then to the cave exhaust. During several experiments, trap NaF-3 was heated to 400°C and the UF_6 was desorbed in a stream of fluorine and then collected in dry-ice-cooled cold traps. The UF_6 was removed from the cold traps by hydrolysis with 20 v/o nitric acid.

The equipment sizes and loading specifications are listed in Table I.

TABLE I. Equipment Size and Loading Specifications

Component	Size		Charge Materials	
	ID, in.	Length, in.	Description	Weight or Volume
Reactor	1.5	14	Alcoa T-61 alumina (28-100 mesh)	700 g
Disengaging Section	4.5	12	-	-
Fixed-bed Filter	2.5	6.5	Alcoa T-61 alumina (see text)	900 g
Condenser	5.0	16	-	-
Scrubber	4.0	60	3-ft-deep 1/2-in. Raschig rings	20 liters (reservoir capacity)
NaF-1 and NaF-2	2.5	26	1/8-in. dehydrofluorinated NaF·HF (Harshaw)	1000 g
NaF-3 and NaF-4	2.5	14	1/8-in. dehydrofluorinated NaF·HF (Harshaw)	500 g
Fluorine Absorption Tower (three sections in series)	3.0	12 per section	1/4-in.-diam activated alumina pellets	1000 g/section
Disposable Filter	3.0	3	Pyrex wool filtering fibre (Owens-Corning No. 3950)	22 g
High-temperature Valves (V1 and V2)	-	-	Research Controls, Tulsa, Oklahoma; nickel, Monel bellows sealed, air operated	-

B. Instrumentation

Because of the experimental nature of the equipment, liberal use was made of thermocouples and pressure gauges. Several thermocouples connected to multipoint recorders were attached to each heated section, and pressure gauges were positioned so that any plugging that might occur could be immediately located. In addition, the system pressure and the pressure drops across the reactor and filter beds were continuously recorded. All pressure taps were purged with nitrogen. The system pressure was sensed by a pressure transmitter with a Monel diaphragm, and

the bed pressure drops were sensed by differential-pressure transmitters. Diluent, purge, and reaction gases were metered through rotameters. The flow-control hardware (valves, rotameters, etc.) and the gas supply cylinders were located in the isolation room adjacent to the cell.

The bed temperature was recorded by three thermocouples in the thermowells inserted in the bed, two being connected to multipoint recorders and the other to a recorder-controller. The bed-temperature controller was provided as a safety measure. In the event of a temperature excursion, the controller closed a pneumatic valve in the reactor gas inlet line thus stopping the reagent flow but still allowing diluent gas to flow and act as a coolant.

In the event of an equipment leak, loss of reaction gas to the cave atmosphere could cause damage to cave components such as manipulators and windows. To avoid such an occurrence, the cave atmosphere was continuously sampled and monitored for HCl or F₂ using a Mine Safety Appliances Billion-Aire Analyzer. The analyzer was situated in the isolation room and was calibrated for 0-25 ppm HCl and 0-25 ppm F₂.

Progress of the hydrochlorination reaction was followed by the use of a Gow-Mac thermal-conductivity cell, which measured the hydrogen concentration in the off-gas stream. A gas sampling point was situated at the exit from the demister, and an off-gas sample was continuously withdrawn to the thermal conductivity cell located in the isolation room. A continuous record of hydrogen concentration in the off-gas permitted the calculation of reaction rate and HCl utilization efficiency and indicated the time at which the reaction was completed.

The rotameter used for fluorine was a glass tube with a stainless-steel spherical float. To reduce the attack on the glass rotameter tube, the fluorine gas was passed through a NaF pellet bed and Pyrex wool before the rotameter tube to remove trace quantities of HF.

C. The Cave Facility and Remote Operations

1. The Cave Facility

An isometric view of the Chemical Engineering Senior Cave Facility⁵ at ANL is shown in Fig. 4. The processing unit is located in Cell A. This part of the cave is shielded for operation with up to 10,000 Ci of 1 MeV gamma. The cell is 7 x 7 ft deep x 12 ft high. The front walls consist of 3-ft-thick, high-density concrete and contain viewing windows, which are composites of glass and zinc bromide about 40 in. thick. Cell B, which is 9 x 7 ft deep x 12 ft high, is used for sample splitting, grinding, pulverizing, and sample storage. A double-door transfer lock on the back wall of this cell connects the cell to a glovebox located in the isolation room B. This

transfer lock is used for the removal of samples as well as for the introduction of reagents. Cell B is shielded for the same level of activity as Cell A. The third cell, Cell C, is used primarily for the repair of the electric manipulators and for the introduction and removal of large equipment items. Cell C, which is 9 x 7 ft deep x 12 ft high, is shielded for 10 Ci of 1-MeV gamma activity.

108-1296

Fig. 4. Chemical Engineering Senior Cave Facility

The cave is a sealed facility, which operates at a pressure about 0.3 in. of water negative to the adjacent operating areas. This negative pressure is maintained by exhausting 2000 cfm of air from Cells A and B. The inlet air is filtered through high-efficiency AEC filters and supplied to Cells A and C. The air exhausted from the cells is filtered through an AEC filter and an activated charcoal filter and finally discharged to the environment through the cave stacks. This air is monitored for alpha and beta activity after leaving the charcoal filter. An auxiliary ventilation system maintains a negative cave pressure with a 10-cfm exhaust. This system is used when more efficient treatment of the cave exhaust is needed. It is also used during solid sampling operations when high air velocities within the cave are undesirable.

Lighting within the cave is provided by 16 mercury-vapor lamps rated at 400 watts each.

A view of the apparatus prior to installation within the cave is shown in Fig. 5. This view shows the mounting of the equipment on two

108-7237

Fig. 5. Process Unit before Installation in Senior Cave

self-supporting racks. Since the cells were "hot" from previous use, it was necessary to install the equipment and connect all the electrical and gas lines using the Model 3 manipulators and 1-ton hoist. After the erection of the apparatus and the performance of a series of shakedown runs outside the cell, the assembly was separated into two halves and each half was taken into Cell C. Each half was moved from Cell C to Cell A using two manipulator hoists to lift the frame at either end. After the second half was brought into Cell A and aligned with the first half, the process-gas lines were connected using Swagelok fittings. Electrical intercon-

nections were made by the use of multiconductor plugs. The power cables and thermocouple cables were brought in through the front shielding wall of Cell A using a stepped wall plug and connected to six multicable electrical plugs mounted on a rack in front of the equipment. The gas supply system was located in the isolation room adjacent to Cell A. The process-gas line and the nitrogen purge lines were brought into the cell through two stepped wall plugs on the back wall of the cell. As each line was fed through the empty wall plug, it was aligned with its mating line on the equipment frame and then connected by a Swagelok fitting. The lines on the equipment frame were rigidly attached and had been prealigned and staggered to facilitate in-cell connections. After the gas-line connections were made and pressure tested, the wall plugs were filled with fine lead shot and sealed. The introduction of the equipment into the cell and its connection to the power and gas supply system were completed in less than three days.

2. Remote Operations

Processing of irradiated fuel requires a high-integrity seal of the reactor filter and auxiliary traps to prevent the escape of volatile fission products and processing gases such as fluorine and HCl to the cell. Of special concern are the high-temperature seals required for the reactor and filter. The initial design of these seals was based on the use of serrated nickel gaskets for the reactor top and filter top. The shakedown tests

210-1102

Fig. 6. Fluid-bed Reactor Discharge Valve

with the apparatus showed that seals could be made using these gaskets, but that the flange gasket surfaces tended to score and make resealing impossible without polishing the flange surfaces. Successful sealing was accomplished by the use of nickel-plated 1/8-in.-diam copper O rings. These gaskets were usable for several experiments before replacement became necessary. When replacement was required, it was necessary to remove the corrosion products from the flange gasket surfaces using metallographic polishing paper attached to holder adapted to the impact wrench. The bottom of the reactor was sealed by the use of a valve with a replaceable Teflon seal (see Fig. 6). Since the radiation resistance of Teflon is poor, the Teflon seal insert was removed and replaced after every "hot" run. No evidence of deterioration of the Teflon insert from radiation or reagent gases was noted during these runs. Other seals on the condenser and NaF traps were made using flat Teflon gaskets, which could be replaced as required. No difficulty was experienced with these seals.

Figure 7 shows a dummy fuel strip being loaded into the reactor. The fuel strip is poised above the reactor opening. The inclined bottle is the receiver for the reactor-bed sample. The sample was taken by blowing out a small amount through a line immersed in the bed via the three-way valve shown.* The filter-flange top is shown with the captive-bolt-lug arrangement used to clamp the flange in place. The pneumatic hose is attached to a vacuum cleaner. The hose removes particulate matter from the apparatus and minimizes dusting when the apparatus is opened, beds are dumped, or cartridges are withdrawn.

Figure 8 shows the use of an impact wrench to seal the condenser flange. The torque imparted to the bolts was controlled from outside

* The primary method of reactor-bed sampling, however, was to dump the entire bed following a run and reduce the bed to a representative fraction using a sample splitter. Several comparisons made between these two methods for gross gamma activity were found to agree closely.

108-7946

Fig. 7. Reactor and Packed-bed Filter, Top View

108-7941

Fig. 8. Impact Wrench Sealing the Condenser

the cell by regulating the supply voltage to the impact wrench. The wrench provided a torque of about 20 to 90 ft-lb. The polyethylene bottle shown was used to contain the dilute HCl, which was used to spray down the walls of the condenser to remove the condensed ZrCl_4 or AlCl_3 . Removal of the top was desirable to insure that all the solids were dissolved. The multi-connector plug in the lower right corner shows the male half of the 52-junction multiconductor plug used for the thermocouple connections.

Figure 9 shows the cartridge containing NaF pellets being removed from the NaF trap. The cartridge-removal tool is clamped on to a bridge welded between two tubes, which extend into the cartridge bed. The tubes are used as thermocouple wells. The adjacent trap shows the top flange sealed in place and the two cartridge-bed thermocouple connections. The glass shields were removed from the pressure gauges just prior to installation of the unit in the cave.

Fig. 9
Removal of Cartridge from
Sodium Fluoride Trap

108-7939

The removal of NaF pellets from a cartridge into a sample-splitter tray using a dumping tool is shown in Fig. 10. The dumping tool is mounted on a movable cart, which was used to provide a bench top

inside Cell A. This item was made movable to provide access to equipment behind it. Figure 11 shows the transfer of a split sample of the reactor bed to a motorized mortar grinder.

Fig. 10

Cartridge-dumping
Tool

108-7940

Fig. 11

Transfer of Reactor-bed Sample
to a Motorized Mortar Grinder

108-9362

D. The Model 3 Master-Slave Manipulators

The cave facility is equipped with four Model 3 Master-Slave Electric Manipulators.⁶ These manipulators are suspended from rails within the cells and are connected to the master arm by an electric cable system. Force-reflecting servomotors drive each of the seven motions of the slave arm in synochronism with the motions of the master arm. The servomotors reflect the slave load forces back to the master. Force reflection can be selected to be 1:1 or 1:3. The tong servo has three force-reflecting ratios of 9:1, 3:1, or 1:1. The load capacity of the slave is 50 lb for 15-min periods or 30 lb for continuous operation. Integral with each slave unit is a 2000-lb hoist with a 10-ft lift. A rail system inside the cells is provided so that all four slave units may be moved to Cell C for repair if required.

E. Sampling and Analysis

1. Irradiated Charges

a. Uranium-Zircaloy

The irradiated material charged to the fluid-bed reactor consisted of eight strips, about $9 \times 9/16$ in., weighing about 270 g, cut from irradiated plates obtained from the Shippingport reactor. The original enrichment of this fuel material was 2.53 a/o ^{235}U irradiated to about 40% burnup and cooled about 5 yr before experimental use. A sample of the charge weighing about 1.3 g was cut from these strips and dissolved in 25 ml HCl-2.5 ml HF, with hydrogen peroxide added to oxidize the uranium. An aliquot of the dissolver solution was then taken and analyzed for uranium and the fission-product elements, as described below.

b. Uranium-Aluminum

Uranium-aluminum alloy fuel tubes were irradiated in the CP-5 reactor for 8 months at an average flux of 5×10^{13} n/cm²-sec. The initial uranium concentration was about 9 w/o, with an initial enrichment of 93%. Estimated burnup was about 50%; cooling time before experimental use was 7 months. The fuel rod was cut into strips about $9 \times 1/2 \times 0.050$ in. Ten strips weighing about 107 g total were used as a charge. Small pieces weighing about 0.4 g were chopped from the ends of the strips and used as samples for the fuel analysis. About 0.8 g of the sample was dissolved in 4:1 Aqua Regia + trace HF under reflux conditions. An aliquot of the dissolver solution was used for uranium and fission-product analyses.

The fuel for two experiments using shorter-cooled fuel (SCAA-3 and -4) were obtained from CP-5 irradiated-fuel rods. The irradiation time was 2 yr with a 3-months cooling time. About 40 g of irradiated fuel was added to 60 g of nonirradiated uranium-alloy (3.69 w/o uranium) to constitute the charge. The irradiated fuel was mixed with nonirradiated fuel to maintain a uranium and activity level loading similar

to the previous two experiments with 7-months-cooled fuel. The sampling and dissolution procedures were similar to the procedures for the 7-months-cooled fuel.

2. Process Sampling

a. Reactor and Filter Beds

The reactor and filter beds, composed of granular alumina, were completely removed from the unit following an experiment and reduced to a manageable size by the use of a sample splitter (conforming to standard ASTM D271). The split portion weighing about 25 g was pulverized using a motorized mortar-pestle. A small part of this sample was then fused with 1:1 sodium carbonate-sodium borate flux with flux-to-sample ratio of 5:1, and then dissolved in 6M HCl. Later investigative work showed that some cesium volatilized during the fusion step.

b. Sodium Fluoride Beds

The sodium fluoride beds were completely discharged from the equipment, and a 25-g sample was obtained from the sample splitter. The 25-g portion was pulverized, and a portion was dissolved in dilute 4:1 HCl-nitric acid of about 3 normal.

c. Activated-alumina Beds

The activated-alumina beds were completely removed from the apparatus, sample-split, and leached with concentrated 4:1 Aqua Regia. The solution was submitted for analysis.

3. Analytical Methods

Assay for radioactive nuclides was made with a sodium iodide well-type scintillation counter with a platinum absorber, or an end-window proportional counter. In all cases, the completeness of separation from other gamma emitters was checked on a gamma spectrometer.

- a. Uranium. The uranium was determined colorimetrically with dibenzoylmethane or fluorophotometrically after its separation from fission products by a hexone extraction.
- b. Beta. An appropriate aliquot of the sample was evaporated to dryness in a 1-in. -diam dish and counted.
- c. Gamma. An aliquot of the sample was diluted to an appropriate volume and counted.

- d. Cerium. A gamma assay was performed after separation of cerium (IV) by extraction with TTA-xylene.
- e. Cesium. A gamma assay was performed after separation by extraction with tetraphenylboron in isoamyl acetate.
- f. Strontium. A beta assay was performed after separation of the other fission products with a ferric hydroxide precipitation and then precipitation of strontium as the carbonate.
- g. Total Rare Earths. A beta assay was performed after separation of rare earths by extraction with di-(2-ethylhexyl) phosphoric acid in hexane.
- h. Antimony. A gamma assay was performed after distillation and collection of antimony as the bromide.
- i. Zirconium. A gamma assay was performed after extraction with di-n-butyl phosphate in toluene. Hydrogen peroxide was used to prevent extraction of niobium.
- j. Niobium. A gamma assay was performed after zirconium extraction with di-n-butyl phosphate in toluene. Niobium value obtained by difference between Zr + Nb and zirconium.
- k. Iodine. A beta assay was performed after separation from other fission products and precipitation as silver iodide.
- l. Ruthenium. A gamma assay was performed after distillation of ruthenium as the tetroxide.
- m. Molybdenum. A colorimetric analysis using thiocyanate was performed.
- n. Technetium. A colorimetric determination with zinc dithiol was performed after distillation from sulfuric acid.
- o. Tellurium. A beta assay was performed after separation from the other fission products by repeated precipitation of tellurium as the metal.

F. Waste Disposal

Both liquid and solid radioactive wastes are generated by these experiments. The liquid wastes, such as the scrubber solution, were pumped

into a 10-gal steel pail and solidified with Portland cement. Solid wastes were loaded directly into 10-gal pails and sealed with a gasketed lid. These pails were then transferred to Cell C, where a protective polyethylene bag, which covered the pail, was removed and the pail transferred out of the cell and placed into a movable lead-shielded pot. The pot was then transported to the Argonne Waste Storage Area.

III. RESULTS AND DISCUSSION

A. Experiments with Nonirradiated Fuel Materials

Before the experimental unit was introduced into the shielded cave, seven experiments were completed with nonirradiated materials outside the cave. The objectives were to test the apparatus, to develop procedures for remote operation, and to follow the uranium distribution for "cold" charges.

The experiments consisted of three runs with 4 w/o uranium-Zircaloy, two runs with 4 w/o uranium-aluminum, and one each with Zircaloy alone and aluminum alone. The conditions for the five uranium-containing runs are summarized in Table II.

TABLE II. Conditions during FBV Processing of Nonirradiated Uranium-alloy Fuels

	SCIZ ^a -1		SCIZ ^a -2		SCIZ ^a -4		SCIA ^b -1		SCIA ^b -2	
HCl Step										
Process Time, hr	14		9		0-2 2-6		6		0-3 3-4	
Av. Bed Temp, °C	400		390		395 505		210		220 250	
Av. Wall Temp, °C	385		375		375 485		200		195 240	
Av. Filter Temp, °C	355		350		350 350		220		210 210	
Inlet HCl Concentration, v/o	42-89		41-85		42-82		22-39		19-29	
Av. Superficial Gas Velocity in Reactor, ft/sec	0.5		0.5		0.6		0.6		0.6 0.4	
Reaction Rate, ^c g/hr	55		44		10 71		d		49 e	
HCl Utilization Eff, %	27		22		4.5 28		d		100 e	
	Start	Final	Start	Final	Start	Final	Start	Final	Start	Final
F ₂ Step										
Bed Temp, °C	270	540	250	525	250	520	275	520	260	515
Wall Temp, °C	255	500	250	500	240	490	255	495	240	490
Filter Temp, °C	305	510	255	510	230	510	280	500	260	495
F ₂ Concentration, v/o	8	63	8	78	8	66	8	83	8	56
Superficial Gas Velocity in Reactor, ft/sec	0.6	0.1 ^f	0.5	0.1 ^f	0.5	0.1 ^f	0.5	0.1 ^f	0.5	0.1 ^f

^aSenior Cave Inactive Zircaloy.

^bSenior Cave Inactive Aluminum.

^cThe reaction rate varied considerably during the experiment. The values shown represent steady rates obtained for significant portions of the time period under consideration. They do not represent overall average values.

^dErratic reaction rate.

^eConstantly decreasing reaction rate and HCl utilization efficiency.

^fBed in static condition.

The uranium distribution for these runs is given in Table III. The significant results may be summarized as follows:

1. The retention of uranium by the reactor bed and the filter bed for all the runs, with the exception of Run SCIZ-4, totaled less than 1% of the uranium charged. The high result obtained for SCIZ-4 is believed to be due to the incomplete chlorination of the uranium that occurred when the hydrochlorination cycle time was shortened to $6\frac{1}{4}$ hr.

TABLE III. Uranium Distribution following FBV Processing of Nonirradiated Uranium-alloy Fuels

Reactor Bed: 700 g of Alcoa T61 alumina, 28-100 mesh
 Filter Bed: 380 g Alcoa T61 alumina, 14-28 mesh, for all runs except Run SCIZ-4
 900 g of Alcoa T61 alumina, 14-28 mesh, for Run SCIZ-4

	Uranium Concentration as Percent of Original Charge				
	SCIZ-1	SCIZ-2	SCIZ-4	SCIA-1	SCIA-2
Charge	100	100	100	100	100
Reactor Bed	0.45	0.46	2.2	0.22	0.13
Filter Bed	0.22	0.11	4.1	0.04	0.10
Condenser	N.A. ^a	3.8	0.20	10.4	0.30
NaF-1 Trap	0.12 ^b	0.13 ^b	0.49	0.20	0.12
NaF-2 Trap	0.40 ^b	0.42 ^b	c	0.11	c
NaF-3 Trap (before desorb)	N.A. ^a	N.A. ^a	92.2	N.A. ^a	N.A. ^a
NaF-3 Trap (after desorb)	0.07	0.19	(0.32) ^d	0.33	0.16
NaF-4 Trap	13.9 ^b	14.5 ^b	0.28	2.34	0.04
Cold Traps	38.2	69.2	(84.5) ^d	60.6	90.3
Fluorine Absorption Tower	4.3	7.6 ^e	(5.6) ^d	9.3 ^e	9.4 ^e
Uranium Balance	58	96	99.5	84	101

^aNot analyzed.

^bAnalyzed following SCIZ-2. Represents an average result for two runs.

^cNaF-2 trap not charged for these runs.

^dThese values are results after desorption of NaF-3 trap and are not included in the uranium balance listed as percent of original charge.

^eAnalyzed following SCIA-2. Represents an average result for three runs.

2. The uranium loss to the condenser during hydrochlorination was reduced significantly by redesigning the filter-bed housing and increasing the bed depth from $4\frac{1}{2}$ to 7 in. In the preliminary runs, where high losses of uranium to the condenser were found, some bypassing of the filter is believed to have occurred. Acceptable uranium loss values of 0.2 and 0.3% were found for Runs SCIZ-4 and SCIA-2 after the trap was modified.

3. High uranium losses to the NaF-4 trap during the preliminary runs occurred because of bypassing of the NaF-3 trap. The NaF pellets are contained in a removable cartridge within the NaF traps. The annulus between the cartridge and the trap was sealed using a fine mesh powder. The initial work used -20 +40 mesh CaF, which permitted

some UF₆ penetrations. The later experiments used -25 +60 NaF and were successful in virtually eliminating bypassing.

4. Cold-trap efficiencies were low in the early runs. This was attributed to partial bypassing of the cold trap. A piping change corrected this deficiency with the resulting improvement shown in the later runs.

5. The uranium balances achieved were considered satisfactory. The final inactive run (SCIA-2), prior to the units being installed in the cave, resulted in high uranium recovery and essentially complete accountability.

B. Experiments with Irradiated Fuel Materials

1. Recovery of Uranium

A comparison of the removal of uranium from the reactor and filter beds for irradiated and nonirradiated uranium alloy fuels is given in Table IV. This comparison shows that the removal of uranium is not

TABLE IV. Comparison of Uranium Removals from Reactor and Filter Beds for Nonirradiated and Irradiated Charges

	Uranium-Zircaloy				Uranium-Aluminum			
	Nonirradiated		Irradiated		Nonirradiated		Irradiated	
	SCIZ-1	SCIZ-2	SCAZ-1	SCAZ-2	SCIA-1	SCIA-2	SCAA-1	SCAA-2
Uranium Charged, g	8.8	8.5	4.9	4.5	7.0	6.95	4.3	4.3
Reactor-bed Alumina, g	736	736	700	700	700	700	700	700
Filter-bed Alumina, g	375	385	900	900	900	900	900	900
Final Uranium Concentration in Reactor Bed, w/o	6×10^{-3}	5.3×10^{-3}	6×10^{-3}	6.7×10^{-3}	2.1×10^{-3}	1.2×10^{-3}	6×10^{-4}	1.7×10^{-3}
Final Uranium Concentration in Filter Bed, w/o	6×10^{-3}	2.3×10^{-3}	2×10^{-3}	1.8×10^{-3}	6.8×10^{-4}	1.7×10^{-3}	8×10^{-5}	1.7×10^{-3}

affected by the presence of fission products or a radiation field since the residual uranium levels for the active runs were as low as those obtained with nonirradiated fuel charges.

The recovery of uranium for the first three runs was 90, 76, and 96%. The recovery of uranium in the cold traps for the last three runs was 96, 65, and 27%. The reason for the low recoveries in the last two runs is not known. Decontamination factors in all cases were based upon the uranium recovered. Therefore it is believed that the values calculated for the last two runs are apt to be biased conservatively (i.e., low).

2. Uranium Decontamination Factors

The decontamination factors obtained for the series of six runs with irradiated fuel materials is shown in Table V. Runs 1 and 2 were made with 5-yr-cooled uranium-Zircaloy, Runs 3 and 4 were made using 7-month-cooled uranium-aluminum, and Runs 5 and 6 were made with 3-month-cooled uranium-aluminum. The general procedure followed for all the runs was the same, except that for the first three runs, sodium fluoride at 100°C was used to collect the uranium; in the last three runs, uranium was collected on sodium fluoride at 150°C, revolatilized, passed through a sintered-metal filter to remove any particulate activities, and collected in a cold trap. For Runs 5 and 6, a MgF_2 trap held at 125°C was interposed between the sodium fluoride product trap and the cold traps. The purpose of this trap was to remove neptunium and technetium activities from the uranium product stream. The decontamination procedure for each run is shown schematically in Figs. 12-15.

TABLE V. Uranium Decontamination Factors Obtained by FBV Processing of Irradiated Uranium-alloy Fuels

Activity	Decontamination Factors ^a					
	Product Collected in NaF-3 Trap			Product Collected in Cold Trap		
	SCAZ-1 Run 1	SCAZ-2 Run 2	SCAA-1 Run 3	SCAA-2 Run 4	SCAA-3 Run 5	SCAA-4 Run 6
Gross γ	5×10^4	2×10^4	5×10^3	2×10^5	2×10^7	3×10^7
Gross β	4×10^4	6×10^3	3×10^4	2×10^5	2×10^6	1×10^6
Ce			7×10^4	3×10^6	3.5×10^7	7×10^6
Sr			9.5×10^3	5×10^6	1×10^7	1×10^7
Cs	5×10^4	2×10^4	3×10^4	3×10^6	4×10^6	4×10^6
Ru	2×10^4	8×10^3	2×10^4	5×10^3	7×10^5	5×10^5
Sb	3×10^3	2×10^4	1×10^3	4×10^5	3.5×10^5	7.5×10^5
Zr			5×10^3	4×10^6	1×10^8	3.5×10^7
Nb			3×10^3	1×10^6	7×10^7	1×10^7
Tc	1.0	1.0	1.5	3	2	0.5
Mo	4	8	5	45		
Te			7×10^2	6×10^4		
Np					3.5	1.3
Pu					6×10^4	3×10^4

^aDecontamination factor = $\frac{\text{activity per gram of uranium in the fuel charge}}{\text{activity per gram of uranium in the product trap}}$

Run Conditions

Charge: Uranium-Zircaloy-2 alloy, 270 g, cooled 5 yr, containing 4.9 g of uranium and 3.3 g of fission products. Original uranium enrichment 93%. $\gamma = 1.7 \times 10^{13}$ c/m, $\beta = 1 \times 10^{13}$ c/m $\sim 1 \times 10^{14}$ d/m.

HCl Step: Reactor bed 400°C, filter bed 350°C, average HCl concentration 40%, total $N_2 + HCl$ flow 5 liters/min at NTP, superficial gas velocity (at 400°C) = 0.54 ft/sec.

Fluorination Step

Time, hr	F ₂ Concentration, v/o	Reactor-bed Temp, °C	Filter-bed Temp, °C	Gas Flow, liters/min NTP
0-1½	8	250-475	270-425	5.5
1½-2	8-75	475-500	425-460	5.5
2-4	75	500	460-485	1.0

Percent of Charge

*Analysis known to be low.

**One run only.

Fig. 12. Distribution of Uranium and Fission Products following FBV Processing of Irradiated 5-yr-cooled Uranium-Zircaloy Alloy--Runs SCAZ-1 and -2

Run Conditions

Charge: Uranium-aluminum alloy, 107 g, cooled 7 months, 4.3 g of uranium and 4.3 g of fission products. Original uranium enrichment 93%,
 $\gamma = 1.2 \times 10^{14}$ c/m, $\beta = 5.1 \times 10^{13}$ c/m $\sim 5 \times 10^{14}$ d/m.

HCl Step: Reactor bed 220-250°C, filter bed 180-250°C, average HCl concentration 20%, total gas flow 7.1 liters/min NTP.

Fluorination Step

Time, hr	Reactor-bed Temp, °C	Filter-bed Temp, °C	F ₂ Concentration, v/o	Gas Flow, liters/min NTP
0-1	260	250	5	6
1-2	260-505	250-485	10	6
2-4	505-520	485-505	75	1

Percent of Charge

*Analysis known to be low.

Fig. 13. Distribution of Uranium and Fission Products following FBV Processing of Irradiated 7-month-cooled Uranium-Aluminum Alloy--Run SCAA-1

Run Conditions

Same as for Run SCAA-1, except for the addition of a desorption step.

Desorption Step

NaF-2 Trap	NaF-3 Trap	Cold Trap	F ₂ Concentration	Gas Rate, NTP
25 → 400°C	400°C	-78°C	75 v/o	2 liters/min

Percent of Charge

*Analysis known to be low.

Fig. 14. Distribution of Uranium and Fission Products following FBV Processing of Irradiated 7-month-cooled Uranium-Aluminum Alloy--Run SCAA-2

Run Conditions

Charge: Both irradiated plus nonirradiated uranium-aluminum alloy charged. The irradiated alloy weighed about 37 g, cooled 3 months, and contained about 1.7 g of uranium and 1.7 g of fission products. The nonirradiated charge weighed about 60 g and contained 2.2 g of uranium. Granular alumina 700 g of 28-100 mesh: $\gamma = 1.5 \times 10^{14}$ c/m, $\beta = 4.3 \times 10^{13}$ c/m $\sim 4.3 \times 10^{14}$ d/m, $^{131}\text{I} - 2.0 \times 10^9$ c/m (4/27/65).

Process Conditions: Similar to conditions for SCAA-2. MgF_2 trap added during desorption step.

Percent of Charge

*The elements listed were detected by gamma spectrometric analysis. This method using a NaI crystal does not distinguish between zirconium and niobium; hence the presence of one or the other or both is represented by Zr/Nb.

Fig. 15. Distribution of Uranium and Fission Products following Processing of Irradiated 3-month-cooled Uranium-Aluminum Alloy--Runs SCAA-3 and -4

In general, the addition of the product revolatilization step increases the uranium decontamination factors by one or more orders of magnitude. Technetium, however, showed a different behavior; the decontamination of uranium from technetium was not improved, and, in one case (Run SCAA-4), an apparent enrichment of technetium in the UF_6 product occurred. This was probably due to poor uranium collection in the cold trap with a corresponding high technetium collection.

The increase in the decontamination factor from molybdenum from 5.0 to 44.6 is ascribed to increasing sodium fluoride product trap temperature from 100 to 150°C. By increasing the sodium fluoride temperature, most of the molybdenum hexafluoride passed unaffected through the trap while the UF_6 was sorbed. This technique for purifying UF_6 streams has been employed at ORNL.

Gamma spectrometric analyses of the uranium product obtained for the last two runs showed that the principle gamma-emitting contaminants were ^{237}U , ^{103}Ru , ^{106}Ru , ^{95}Zr , and ^{95}Nb with the preponderant activity due to ^{237}U . This result suggests that further improvements in decontamination techniques will not be of value in processing high-burnup, short-cooled fuels (~3 months) since the gamma-activity level will be determined by ^{237}U . Improvements in the fission-product traps and filtration technique will be of value in processing longer-cooled fuels, since the ^{237}U activity decays fairly rapidly ($T_{1/2} = 6.7$ days). For example, an additional $1\frac{1}{2}$ months cooling would decrease the ^{237}U contribution by several orders of magnitude, and therefore the ruthenium and niobium gamma contribution would predominate. Further improvements to increase the decontamination factor from the volatile fission products ruthenium and niobium are believed to be achievable by a more optimum use of NaF. Some work to study the effect of flowrate, temperature, and methods of sorbent activation upon ruthenium and niobium removal in a flow system would be required.

3. Distribution of Fission Products and Neptunium

The charge data, the run conditions, and the distribution of the fission products in the various process streams for the six runs with irradiated metal alloy fuels are given in Figs. 12-15. The values shown are given as the percent of the charge found in each process stream. For example, after the HCl step in Runs 1 and 2 (Fig. 12), 2.7% of the antimony charged to the fluid-bed reactor was found in the condenser. Following the fluorination step, 82% of the uranium charged to the reactor was found in the 100°C NaF trap along with 0.004% of the gamma activity charged. The analytical data for the first six runs are summarized in Tables VI-XI. Where the analyses were performed colorimetrically, the analyses are given in grams; where radiochemical analyses were performed, the values are given in counts/min (c/m). Decay corrections were necessary

for the uranium-aluminum runs, and normalization dates were chosen to avoid making corrections to fission-product mixtures. The fission products and the amounts of each that volatilized from the fluid-bed reactor during the HCl step and the fluorine step are shown in Table XII. To permit calculation of the composition of the charge and the various process streams in terms of their gamma-active isotopes, the gamma-active isotopes were normalized to the date the gross gamma count was made. These compositions are given in Tables XIII and XIV. The following discussion is divided into two parts; the first deals with fission-product distribution following the hydrochlorination step, the second concerns the fission-product distribution following the fluorination step.

TABLE VI. Summary of Analyses for Irradiated Uranium-Zircaloy--Run SCAZ-1^a

Sample	U, g	Gross γ , c/m	Gross β , c/m	Sr(β), c/m	Ru(γ), c/m	Cs(γ), c/m	Sb(γ), c/m	Mo, g	Tc, g	Gamma Spectrometric Analyses ^b
Charge	4.90	1.4×10^{13}	1.1×10^{13}	2.7×10^{12}	1.4×10^{11}	1.45×10^{13}	1.9×10^{11}	0.455	0.086	Cs, CePr
Reactor Bed	0.04	5.2×10^{12c}	4.0×10^{12}	1.3×10^{12}	3.4×10^{10}	4.7×10^{12c}	2.7×10^{10}			Cs, CePr
Filter Bed	0.018	2.0×10^{12c}	1.3×10^{12}	3.0×10^{11}	4.6×10^{10}	1.9×10^{12c}	1.1×10^{10}			Cs, CePr
Condenser	0.02	9.0×10^9	5.6×10^9				5.2×10^9			Sb, Cs, CePr
Scrubber	0.001	2.1×10^8	8.5×10^7				2.1×10^8			Sb
400°C NaF	0.018	1.0×10^{11}	1.0×10^{11}		8.5×10^8		4.8×10^{10}			CePr, Cs, Sb
100°C NaF	4.40	3.3×10^8	3.0×10^8	6.5×10^7	8.5×10^6	2.6×10^8	6.7×10^7	0.12	0.065	CePr, Cs
25°C NaF	0.04	1.4×10^{10}	2.4×10^{10}					0.17		CePr, Cs, Ru, Sb
Percent of Charge Recovered	93	45 ^c	52	59	57	46 ^c	48	64	77	

^aWhere no value is listed in the table, no analysis was performed.

^bCePr = ¹⁴⁴Ce-Pr; Cs = ¹³⁴Cs and ¹³⁷Cs; Sb = ¹²⁵Sb; Ru = ¹⁰⁶Ru.

^cRecovery known to be low because of cesium loss during reactor- and filter-bed analyses.

TABLE VII. Summary of Analyses for Irradiated Uranium-Zircaloy--Run SCAZ-2^a

Sample	U, g	Gross γ , c/m	Gross β , c/m	Sr(β), c/m	Ru(γ), c/m	Cs(γ), c/m	Sb(γ), c/m	Mo, g	Tc, g	Gamma Spectrometric Analyses ^b
Charge	4.5	1.7×10^{13}	1.0×10^{13}	2.8×10^{12}	1.5×10^{11}	1.6×10^{13}	2.0×10^{11}	0.48	0.076	CePr, Cs
Reactor Bed	0.047	6.2×10^{12c}	4.0×10^{12}	1.3×10^{12}	4.6×10^{10}	5.8×10^{12c}	1.3×10^{10}			CePr, Cs
Filter Bed	0.016	2.1×10^{12c}	1.2×10^{12}	2.7×10^{11}	3.7×10^{10}	2.0×10^{12c}	8.2×10^9			CePr, Cs, Ru
Condenser	0.017	1.1×10^{10}	1.2×10^9							CePr, Cs, Sb
Scrubber	0.011	2.2×10^{10}	7.7×10^8						0.002	Sb, Cs
400°C NaF	0.022	1.2×10^{11}	6.0×10^9		4.8×10^8		1.0×10^{11}			Sb
100°C NaF	3.44	1.05×10^9	1.7×10^9	5.7×10^8	2.0×10^7	1.0×10^9	1.1×10^7	0.059	0.060	CePr, Cs, Ru
25°C NaF	0.058	4.1×10^8	8.4×10^8					0.056		CePr, Cs, Ru
Act. Alumina		1.3×10^{10}	1.5×10^{10}							CePr, Cs, Te, ^d Ru
Percent of Charge Recovered	80	49 ^c	53	56	55	49 ^c	61	24	81	

^aWhere no value is listed in the table, no analysis was performed.

^bCePr = ¹⁴⁴Ce-Pr; Cs = ¹³⁴Cs and ¹³⁷Cs; Sb = ¹²⁵Sb; Ru = ¹⁰⁶Ru.

^cRecovery known to be low because of cesium loss during reactor- and filter-bed analyses.

TABLE VIII. Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-1

Sample	U, g	γ^a , c/m	β^b , c/m	$Sr^b(\beta)$, c/m	$Cs^a(\gamma)$, c/m	$Ce^a(\gamma)$, c/m	$Ru^a(\gamma)$, c/m	$Zr^a(\gamma)$, c/m	$Nb^a(\gamma)$, c/m	$Te^a(\beta)$, c/m	$Sb^a(\gamma)$, c/m	Mo, g	Tc, g	Gamma Spectrometric Analyses ^c
Charge	4.28	1.2×10^{14}	7.4×10^{13}	2.5×10^{12}	1.5×10^{13}	5.1×10^{12}	5.3×10^{12}	3.2×10^{12}	4.5×10^{13}	9.6×10^{10}	2.9×10^{11}	0.250	0.062	CePr, Zr/Nb, Cs, Ru
Reactor Bed	0.004	1.1×10^{13}	3.6×10^{13}	1.7×10^{12}	3.1×10^{12}	2.8×10^{12}	2.3×10^{12}	6.5×10^{11}	1.2×10^{12}					CePr, Ru, Cs, Zr/Nb
Filter Bed	0.0007	3.0×10^{12}	4.3×10^{12}	1.6×10^{11}	5.7×10^{11}	4.3×10^{11}	7.9×10^{11}	1.3×10^{11}	4.5×10^{11}					CePr, Ru, Cs, Zr/Nb
Condenser		2.9×10^{13}	1.4×10^{10}					1.6×10^{13}	1.9×10^{13}	1.4×10^8	1.4×10^8	0.003		Zr/Nb
Scrubber		4.7×10^{10}	2.8×10^9					2.3×10^9	1.1×10^{10}	2.8×10^{10}	1.5×10^{10}	0.001		Sb, Zr/Nb
400°C NaF	0.02	4.3×10^{12}	8.2×10^{12}		1.4×10^9		1.2×10^{10}	7.0×10^{11}	2.0×10^{12}					Zr/Nb, Cs
100°C NaF	4.1	2.4×10^{10}	2.5×10^9	2.3×10^8	5.5×10^8	7.0×10^7	3.0×10^8	6.8×10^9	1.4×10^{10}	1.5×10^8	2.5×10^8	0.050	0.040	Zr/Nb, CePr, Cs
25°C NaF	0.28	1.0×10^{10}												CePr, Ru, Zr/Nb
Act. Alumina		8.5×10^9	1.8×10^{10f}							4.8×10^{10}				Te, CePr, Zr/Nb
Percent of Charge Recovered	103	39 ^d	66	74	25 ^d	64	59	53	53	51	e	e	65	

^aNormalized to 2/27/65.^bNormalized to 5/1/65.^cCePr = ^{141}Ce and ^{144}Ce -Pr, Zr/Nb = ^{95}Zr and/or ^{95}Nb , Cs = ^{134}Cs and ^{137}Cs , Ru = ^{103}Ru and ^{106}Ru , Te = ^{125m}Te and ^{129m}Te .^dRecovery known to be low due to loss of cesium during analyses of reactor and filter beds.^eNot determined.^fValue probably low.

TABLE IX. Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-2

Sample	U, g	γ^a , c/m	β^b , c/m	$Sr^b(\beta)$, c/m	$Cs^a(\gamma)$, c/m	$Ce^a(\gamma)$, c/m	$Ru^a(\gamma)$, c/m	$Zr^a(\gamma)$, c/m	$Nb^a(\gamma)$, c/m	$Te^c(\beta)$, c/m	$Sb^a(\gamma)$, c/m	Mo, g	Tc, g	Gamma Spectrometric Analyses ^c
Charge	4.32	1.1×10^{14}	6.9×10^{13}	2.9×10^{12}	1.5×10^{13}	4.8×10^{12}	4.4×10^{12}	2.3×10^{13}	3.5×10^{13}	3.5×10^{10}	2.9×10^{11}	0.250	0.062	
Reactor Bed	0.012	1.0×10^{13}	3.1×10^{13}	1.9×10^{12}	3.3×10^{12}	2.8×10^{12}	1.9×10^{12}	2.1×10^{11}	4.2×10^{11}	4.2×10^{11}	7.0×10^9	0.015		CePr, Ru, Cs, Zr/Nb
Filter Bed	0.014	2.8×10^{12}	4.9×10^{12}	1.9×10^{11}	8.5×10^{11}	3.6×10^{11}	8.2×10^{10}	1.4×10^{11}	3.3×10^{11}		3.6×10^9	0.015		CePr, Ru, Cs, Zr/Nb
Condenser		3.8×10^{13}	6.8×10^{11}					1.8×10^{13}	2.7×10^{13}	9.0×10^9	2.0×10^9	0.005		Zr/Nb, Sb
Scrubber		5.0×10^{10}	5.4×10^9					1.8×10^8	8.2×10^9	2.0×10^8	2.6×10^{10}	0.0008		Te, Sb, Zr/Nb
400°C NaF	0.019	2.2×10^{13}	2.4×10^{11}		1.0×10^9		1.9×10^{10}	1.2×10^{12}	1.4×10^{13}		2.7×10^{11}			Zr/Nb, CePr, Sb
150°C NaF ^e	0.038	5.8×10^{11}	2.0×10^{10}											Zr/Nb
25°C NaF	0.23	4.7×10^{10}	2.6×10^9									0.022	<0.022	Ru, Zr/Nb
Act. Alumina		1.1×10^{11}	2.1×10^{10}							2.0×10^{10}				Sb, Te, Ru, Zr/Nb
Cold Trap	4.14	6.4×10^8	3.2×10^8	6.4×10^5	5.6×10^6	1.9×10^6	6.2×10^8	7.5×10^6	3.3×10^7	5.9×10^5	8.0×10^5	0.006	0.022	Ru, Zr/Nb, CePr
Percent of Charge Recovered	103	69 ^f	54	70	28 ^f	66	45	85	118	58	106	25	<38	

^aNormalized to 3/17/65.^bNormalized to 5/16/65.^cNormalized to 7/14/65.^dCePr = ^{141}Ce and ^{144}Ce -Pr, Ru = ^{103}Ru and ^{106}Ru , Cs = ^{134}Cs and ^{137}Cs , Zr/Nb = ^{95}Zr and/or ^{95}Nb , Sb = ^{125}Sb , Te = ^{125m}Te and ^{129m}Te .^eAnalyses after uranium desorption step.^fRecovery known to be low because of loss of cesium during analyses of reactor and filter bed

TABLE X. Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-3^a

Sample	Y, c/m	β, c/m	Ce(γ), c/m	Cs(γ), c/m	Sb(γ), c/m	Ru(γ), c/m	Zr(γ), c/m	Nb(γ), c/m	Sr(β), c/m	Np(α), c/m	Tc, g	Gamma Spectrometric Analyses ^b
Charge	1.1×10^{14}	3.8×10^{13}	3.6×10^{12}	6.0×10^{12}	1.1×10^{11}	6.3×10^{12}	3.3×10^{13}	4.6×10^{13}	1.8×10^{12}	3.9×10^6	0.023	CePr, Ru, Zr/Nb
Cold Trap	4.7×10^6	2.4×10^7	6.5×10^4	1.0×10^6	1.6×10^5	7.2×10^6	2.0×10^5	4.3×10^5	8.8×10^4	7.1×10^5	0.008	U, Ru, Zr/Nb

^aRun date 4/20/65, gamma analyses normalized to 6/17/65.^bCePr = ¹⁴⁴Ce-Pr, Ru = ¹⁰³Ru and ¹⁰⁶Ru, Zr/Nb = ⁹⁵Zr and/or ⁹⁵Nb, U = ²³⁷U.TABLE XI. Summary of Analyses for Irradiated Uranium-Aluminum--Run SCAA-4^a

Sample	Y, c/m	β, c/m	Ce(γ), c/m	Cs(γ), c/m	Sb(γ), c/m	Ru(γ), c/m	Zr(γ), c/m	Nb(γ), c/m	Sr(β), c/m	Np(α), c/m	Tc, g	Gamma Spectrometric Analyses ^b
Charge	8.4×10^{13}	3.0×10^{13}	2.7×10^{12}	5.2×10^{12}	1.0×10^{11}	5.5×10^{12}	2.9×10^{13}	4.1×10^{13}	1.5×10^{12}	3.4×10^6	0.020	CePr, Ru, Zr/Nb
Cold Trap	2.4×10^6	2.3×10^7	1.1×10^5	3.2×10^5	1.3×10^5	2.9×10^6	2.1×10^5	1.1×10^6	3.0×10^4	7.1×10^5	0.011	U, Ru, Zr/Nb

^aRun date 4/27/65, gamma analyses normalized to 6/28/65.^bCePr = ¹⁴⁴CePr, Ru = ¹⁰³Ru and ¹⁰⁶Ru, Zr/Nb = ⁹⁵Zr and/or ⁹⁵Nb, U = ²³⁷U.

TABLE XII. Fission Products Volatilized and Collected Downstream of Packed-bed Filter

Element	HCl Step, Percent of Charge				Element	Fluorine Step, Percent of Charge		
	SCAZ-1 and -2	SCAA-1	SCAA-2	SCAA-3 and -4		SCAZ-1 and -2	SCAA-1	SCAA-2
Sb	2.8	5.7	9.7	c	Sb	37.5	31	93
Ru	nil ^a	nil ^a	nil ^a	c	Ru	0.45	0.23	0.6
Zr	b	48.7	64	c	Zr	b	2.2	4.4
Nb	b	44.8	61	c	Nb	b	4.8	30
Mo	c	1.8	2.3	c	Mo	43.5	c	c
Tc	2.7	c	c	c	Tc	77	64.5	35
Te	c	0.34	0.85	c	Te	c	50	57
I	c	c	c	74				

^aNot detected by gamma spectrometric analysis.^bInsufficient present in charge for analysis.^cNot determined.

TABLE XIII. Composition of Charge and Process Streams in Terms of Their Gamma-active Fission Products--Runs SCAZ-1 and -2

	Total γ , c/m	Percent of Total Gamma			
		^{137}Cs	^{125}Sb	^{106}Ru	Remainder
Run SCAZ-1					
Charge	1.6×10^{13}	90.7	1.2	0.9	7.2 ^a
Reactor Bed	5.2×10^{12}	90.5	0.5	0.7	8.3 ^a
Filter Bed	2.0×10^{12}	95.0	0.5	2.3	2.2 ^a
400°C NaF	1.0×10^{11}	N.A.	48	0.8	51.2 ^b
100°C NaF	3.3×10^8	78.8	20.3	2.6	~0
Condenser	9.0×10^9	N.A.	57.8	N.A.	42.2 ^b
Scrubber	2.1×10^8	N.A.	100	N.A.	0
Run SCAZ-2					
Charge	1.7×10^{13}	94.0	1.2	0.9	3.9 ^a
Reactor Bed	6.2×10^{12}	93.7	0.2	0.7	5.4 ^a
Filter Bed	2.1×10^{12}	95.0	0.4	1.7	2.9 ^a
400°C NaF	1.2×10^{11}	N.A.	83.2	0.4	16.4 ^c
100°C NaF	1.1×10^9	95.2	1.0	1.9	1.9 ^a
Condenser	1.1×10^{10}	N.A.	N.A.	N.A.	N.A.
Scrubber	2.2×10^{10}	N.A.	N.A.	N.A.	N.A.

^aSome or all due to $^{144}\text{CePr}$.^b ^{134}Cs and ^{137}Cs plus $^{144}\text{CePr}$.^c ^{125}Sb only activity detected by gamma spectrometric analysis.

TABLE XIV. Composition of Charge and Process Streams in Terms of Their Gamma-active Fission Products--Runs SCAA-1 and -2

	Total γ , c/m	Percent of Total Gamma Activity						
		Nb ^a	Zr ^a	Cs ^a	Ru ^a	Ce ^a	Sb ^a	Remainder
SCAA-1								
Charge	1.2 x 10 ¹⁴	37.4	26.8	12.5	4.4	4.2	0.2	14.5 ^b
Reactor Bed	1.1 x 10 ¹³	10.9	5.9	28.2	21.0	25.5	N.A.	8.5 ^b
Filter Bed	3.0 x 10 ¹²	15.0	4.3	19.0	26.3	14.3	N.A.	21.1 ^b
400°C NaF	4.3 x 10 ¹²	46.5	16.3	0.03	0.3	N.A.	N.A.	36.9 ^b
100°C NaF	2.4 x 10 ¹⁰	58.2	28.8	2.3	1.2	0.3	1.0	8.2 ^b
SCAA-2								
Charge	1.1 x 10 ¹⁴	33.0	21.7	14.2	4.2	4.5	0.3	22.1 ^b
Reactor Bed	1.0 x 10 ¹³	4.2	2.1	33.0	19.0	28.0	0.07	13.7 ^b
Filter Bed	2.8 x 10 ¹²	11.8	5.0	30.3	2.8	12.9	0.1	38.1 ^b
Condenser	3.8 x 10 ¹³	71.0	47.3	N.A.	N.A.	N.A.	0.005	None
Scrubber	5.0 x 10 ¹⁰	16.4	0.4	N.A.	N.A.	N.A.	52	31.2 ^b
400°C NaF	2.2 x 10 ¹³	61.5	5.5	0.004	0.09	N.A.	1.2	31.7 ^c
Cold Trap	6.4 x 10 ⁸	5.1	1.2	0.9	96.7	0.3	0.1	None

^aNb = ^{95}Nb , Zr = ^{95}Zr , Cs = ^{134}Cs and ^{137}Cs , Ru = ^{103}Ru and ^{106}Ru , Ce = ^{141}Ce and $^{144}\text{Ce-Pr}$, Sb = ^{125}Sb .^bCalculational and/or analytical discrepancy.^cSmall amount of $^{144}\text{CePr}$.

a. Distribution following Hydrochlorination Step

The activities found to be essentially nonvolatile during the hydrochlorination step were cerium, cesium, and ruthenium. Trace amounts of cerium and cesium were found in the condenser and scrubber following the runs with 5-yr-cooled uranium-Zircaloy. This is believed to be due to the entrainment of small amounts of these activities, in the gas stream leaving the reactor, which were not completely removed by the packed-bed filter. These activities (cerium and cesium) were not found in the condenser or scrubber by gamma spectrometric analyses following the runs with short-cooled uranium-aluminum, probably because of the masking effect of the large amounts of ^{95}Zr and ^{95}Nb present.

The activities that were slightly volatile during hydrochlorination were Sb, Mo, Tc, and Te (see Table XII). The amounts of these activities that volatilized and were collected downstream of the packed-bed filter ranged from about 0.3 to 10% of the charge activity.

The activities that were predominantly volatile during hydrochlorination were Zr, Nb, Kr, and I. Table XII shows the collection of zirconium and niobium following hydrochlorination. Some partition of zirconium and niobium during hydrochlorination appears to occur from a consideration of the large amount of niobium collected during fluorination. This can be seen especially in Run SCAA-2 (Table XII), where about 30% of the niobium was found downstream of the packed-bed filter following fluorination. As shown in Figs. 13 and 14, only a small amount (1-3%) of the zirconium and niobium remains behind the reactor and filter beds.

The overall recovery of zirconium and niobium as shown in Tables VIII and IX ranges from 53 to 118% and indicates that the preponderant amounts of both zirconium and niobium volatilize during hydrochlorination. An indication of the release of krypton during both process steps was obtained by the use of a beta monitor located in the cave stack. This monitor had been previously calibrated by releasing known amounts of ^{85}Kr to the cave atmosphere. The results of the measurements made during the six "hot" runs showed that essentially 100% of the krypton is released to the stack during the hydrochlorination step. During the fluorination, the activity level in the stack returned to the normal background level.

The last two runs (Runs 5 and 6) were made with 3-month-cooled fuel to follow radioactive ^{131}I . Analyses showed that 66% of the iodine charged to the reactor was collected in the scrubber following the HCl step of Run 5, and 93% was collected for run 6. A trace amount of ^{131}I was found in the activated alumina following the fluorination step. Stack-gas monitoring showed that less than 1% of the ^{131}I was released to the stack during the HCl step and also less than 1% during the fluorination step. These results lead to the conclusion that the bulk of the iodine is released during hydrochlorination and can be efficiently removed by a caustic scrubber (7 w/o NaOH was used in these experiments). A small amount remained in the reactor following hydrochlorination.

b. Distribution following Fluorination Step

The work with the irradiated fuels showed that only trace quantities of cesium and cerium were found downstream of the packed-bed filter. Strontium analyses downstream of the packed-bed filter were not obtained, except for the product trap. The bulk of the strontium charged was recovered with the reactor and filter beds.

The fission products that are partially or completely volatilized during the fluorination step are discussed below.

(1) Ruthenium. As shown in Table XII ruthenium appears to be only slightly volatile under the fluorination conditions. The amount volatilized for the first four runs ranged from 0.2 to 0.6% of that charged to the reactor. The ruthenium downstream of the packed-bed filter was almost entirely collected by the 400°C NaF pellet traps.

(2) Antimony. About 90% or more of the antimony remained in the reactor bed following hydrochlorination. Most of this residue was volatilized during the fluorination step and was almost completely retained by the 400°C NaF trap. A small residue (3-16%) remained in the reactor and filter beds following fluorination.

(3) Zirconium and Niobium. As already noted, the bulk of the zirconium and niobium was removed before fluorination during the hydrochlorination step. As shown in Table XII, 2 to 4% of the zirconium was downstream of the packed-bed filter. This amount of activity, which must pass through the packed-bed filter, raises a question as whether the zirconium is a particulate solid or a gaseous species. A calculation indicated that if the vapor pressure of ZrF_4 in the gas leaving the reactor is about 4% of its saturation value (ZrF_4 v.p. = 0.028 mm Hg at 550°C), sufficient ^{95}Zr would be volatilized to account for the zirconium activity collected by the 400°C NaF trap. It appears likely that the zirconium movement is due to volatilization; hence its separation from volatile uranium hexafluoride depends upon efficient sorption rather than filtration.

As shown in Fig. 14, about 30% of the niobium volatilized during fluorination and was collected by the 400°C NaF trap. The reactor-bed analysis following fluorination showed less than 1% of the zirconium and niobium remained. These two results suggest that a partition between zirconium and niobium occurs during the HCl step; i.e., a smaller amount of the niobium forms a volatile chloride. The niobium that remains following chlorination readily forms a volatile fluoride and is almost entirely removed during fluorination.

(4) Technetium. Technetium closely follows uranium in the processing steps. Only 3% of technetium volatilized during the hydrochlorination step. Following fluorination, the bulk of the technetium collected with the UF_6 in the 100°C NaF traps. This result shows that little or no technetium was removed from the gas stream by the 400°C NaF trap. Desorption of the uranium and technetium from the NaF product traps and subsequent cold trapping resulted in some partition between uranium and technetium, as indicated by decontamination factors of 3 and 2 obtained in Runs 4 and 5 (see Table V). The result obtained in Run 6, in which an apparent enrichment of technetium occurred in the product uranium, is probably the result of obtaining a poor uranium yield for this experiment and should be disregarded.

(5) Molybdenum. Less than 3% of the molybdenum was removed from the fluid-bed reactor following hydrochlorination. The work with uranium-Zircaloy showed that the bulk of the molybdenum volatilized during fluorination and was distributed largely between the 100°C NaF trap and the 25°C NaF trap. Results of a run with uranium-aluminum alloy (Fig. 13) showed that about 20% of the molybdenum was trapped with the uranium in the 100°C NaF trap. As shown in Fig. 14, about 2% was collected with the uranium when an additional desorption step was employed following collection on 150°C NaF. About 12% (see Fig. 14) was found in the reactor and filter beds, indicating that the removal of molybdenum is not complete under these processing conditions.

(6) Tellurium. Less than 1% of the tellurium volatilized during the hydrochlorination step. The bulk of the tellurium volatilized during the fluorination, passed through the 400°C NaF, 100/150°C NaF, and 25°C NaF traps, and collected on the activated-alumina trap. This trap was used principally to remove the excess fluorine from the process off-gas before its discharge to the cave stacks. The alumina-fluorine reaction results in a temperature gradient inside the trap from about 25 to 600°C; hence the collection temperature for the volatile telluride is not known. Stack-gas monitoring showed that only trace amounts of tellurium were present, which indicated that the alumina was highly efficient for the removal of tellurium. Only small amounts of tellurium collected with the uranium. About 0.14% of the tellurium was collected with the uranium (see Fig. 12) when a 100°C NaF trap was employed; 0.0017% was retained with the uranium when a desorption step was employed (see Fig. 14).

(7) Neptunium. Complete neptunium analyses were not performed, but uranium-product analyses for the last two runs showed that about 21% of the neptunium charged was collected with the uranium (see Fig. 15).

(8) Plutonium. Plutonium analyses were performed on the uranium product for two runs with irradiated uranium-aluminum alloy. The decontamination factors obtained averaged about 5×10^4 .

4. Use of MgF_2 for Removal of Technetium and Neptunium

Traps containing MgF_2 have been successfully employed to separate the volatile fluorides of technetium and neptunium from UF_6 .⁷ Two tests were made in which a small MgF_2 pellet bed (100 g) at 130°C was placed upstream of the cold trap to evaluate trapping of neptunium and technetium during UF_6 desorption from the 150°C NaF traps (see Fig. 15). The MgF_2 pellets were of the type used in studies in which high removals of technetium from UF_6 were obtained.⁸ An analysis of the MgF_2 after the run showed about 3.1% of the technetium, 4.5% of the neptunium and 2.5% of the uranium were removed. Since flow conditions and pellet pretreatment were different from the tests reported in Ref. 8, no conclusion regarding the efficiency of MgF_2 for technetium or neptunium removal from UF_6 should be drawn from these tests.

5. Gamma Composition of Process Streams

For shielding purposes, it is useful to know the gross gamma level of each process stream and a classification of the gross activity level in terms of its individual fission-product contributors. Calculations made for the first four runs are shown in Tables XIII and XIV. The first two runs (see Table XIII) used 5-yr-cooled uranium-Zircaloy. The effect of this long cooling is shown in the charge composition, which indicates that about 90% of the gross gamma activity is contributed by ^{137}Cs . The

composition of the gamma activity found in the product trap is shown to be 78 and 95% ^{137}Cs . This result suggests that considerable reduction in product activity level would be achieved by improvements in the filtration of the process off-gas leaving the fluid-bed reactor. The two runs with 7-month-cooled uranium-aluminum alloy (Table XIV) show a charge composition that has $^{95}\text{Zr-Nb}$ as the principal gamma contributor. An examination of the 100°C NaF product activity (SCAA-1) shows $^{95}\text{Zr-Nb}$ to be the principal contaminant; the next run (SCAA-2) shows the effect of revolatilizing the uranium product. The gross gamma activity was reduced by more than an order of magnitude, a good separation from $^{95}\text{Zr-Nb}$ was achieved, and ^{103}Ru and ^{106}Ru were left as the principal gamma contributors. The principal contributor to the condenser activity was $^{95}\text{Zr-Nb}$ (Table XIV, SCAA-2) and ^{125}Sb was the predominant gamma-active species in the scrubber.

6. Fission-product Balances

The uranium, gross beta, gross gamma, and individual fission-product balances are listed in Tables VI-IX. The fission-product recoveries ranged from 46 to 81% for the uranium-Zircaloy runs, and 25 to 118% for the uranium-aluminum runs. The lowest values were obtained for the cesium balances. Investigative work showed that substantial losses of cesium occurred during the fusion of the reactor- and filter-bed sample with sodium borate-sodium carbonate at about 1000°C . Disregarding the cesium values, the balances range from 51 to 118% for these latter two runs.

Balances less than 100% raise questions of pragmatic importance, such as whether substantial amounts of activity are deposited within the processing equipment or if significant quantities of activity are being discharged with the process off-gas. Some work has been directed to these questions. Experiments were performed in which an inactive charge was processed in the equipment to determine the process-stream contamination due to residual activity levels in the apparatus. One such run following Run SCAA-2 showed that the reactor bed and the filter bed become contaminated to a gamma level of about 5% of that observed in the beds after the "hot" run. Another inactive run following Run SCAA-4 showed a contamination level of about 4% for the reactor bed but 75% for the filter bed. While the value 75% appears high, it represents only 1.3% (see Fig. 15) of the gamma charged during Run SCAA-4. Work with aqueous decontaminating solutions on the process line leading from the packed-bed filter to the first NaF trap showed a gamma-activity pickup equivalent to 30% of the previous hot-run charge. The activity within this process line represented the accumulation from 10 hot runs; hence an average contribution is about 3% per run. Aqueous decontamination of the packed-bed filter, which resulted in a radiation level decrease of a factor of two, showed a pickup of less than 2% of the previous hot-run gamma charge.

The process off-gas was discharged into the cell, where it was diluted with 2000 cfm of ventilation air and carried into the cave-stack system. The diluted process off-gas was filtered through a high-efficiency AEC-type filter, passed through an activated charcoal filter, checked for alpha and beta activities by two activity monitors, and discharged through the cave stacks to the atmosphere. The primary and secondary filters were monitored for gamma activity following the experimental work. The maximum radiation level increase recorded on the primary filter was about 1 R/hr at 2 in., which represents less than 1% of the gamma charge for the uranium-aluminum runs. The radiation-level increase on the secondary filter was trivial. These results suggest that the sum of the gamma accumulation within the equipment and the gamma loss to the stack gas during any run is probably less than 10%, and that the disparity in the fission-product balances for these runs is not due primarily to deposition within the equipment or to off-gas loss. These disparities probably are more related to sampling inaccuracies and analytical errors and losses. The values reported, however, show what is believed to be a reasonable consistency and provide a substantially accurate description of fission-product and actinide-element distribution within the process equipment.

IV. SUMMARY AND CONCLUSIONS

The experimental work related to the fluid-bed fluoride volatility processing of irradiated highly-enriched uranium alloy on a bench scale has been completed. The results of this work show:

1. The retention of uranium in the reactor bed and filter bed following the processing of irradiated uranium-Zircaloy or uranium-aluminum alloy was similar to that found in processing nonirradiated fuel alloys. It can be concluded that the results obtained regarding the removal and recovery of uranium in the bench-scale and pilot-plant work with nonirradiated uranium-alloy fuel materials can be validly applied to irradiated fuels.
2. The uranium decontamination levels achieved in the final two runs were high and such that the preponderant gamma activity in the uranium product was due to the uranium isotope ^{237}U . Gross decontamination from gamma activity was greater than 10^7 , and that from beta activity was greater than 10^6 .
3. The decontamination factors for the activities Ce, Sr, Cs, Ru, Sb, Zr, and Nb ranged from 3.5×10^5 to 1.0×10^8 for the final two experiments. A decontamination factor of 5.9×10^4 for tellurium was obtained for one run with 7-month-cooled uranium-aluminum alloy. The plutonium decontamination factor for the last two runs averaged 5×10^4 . Decontamination factors of 44.6, 2.9, and 3.5 were obtained for Mo, Tc, and Np, respectively.
4. Distribution of fission products following hydrochlorination showed the activities Ce, Cs, Sr, and Ru to be essentially nonvolatile. The activities that were slightly volatile ($<10\%$) were Sb, Te, and Tc. The activities that were predominantly volatile ($>50\%$) were Zr, Nb, I, and Kr.
5. Iodine and krypton volatilized essentially completely during the hydrochlorination step of the process. A caustic scrubber was successful in removing iodine from the process off-gas stream. The krypton was allowed to discharge to the atmosphere.
6. Distribution of the fission products following the fluorination step showed that the activities Ce, Cs, and Sr are essentially nonvolatile and are not removed from the reactor-filter beds. Ruthenium was essentially nonvolatile with less than 1% volatilizing and collecting in the fission-product trap. A few percent of zirconium was transported, apparently by volatilization, from the reactor. The activities that were preponderantly volatile ($>50\%$) were Nb, Mo, Tc, Sb, and Te. Sufficient analyses were not performed to establish the complete behavior of neptunium; however, 21% of the charged neptunium was found with the uranium product.
7. Tellurium was completely removed from the process off-gas during the fluorination step by the use of an activated alumina trap.

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