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FLUORIDE VOLATILITY PROCESSING SEMIANNUAL PROGRESS REPORT FOR PERIOD ENDING NOVEMBER 30, 1966

R. P. Milford
G. I. Cathers
R. W. Horton
W. H. Carr

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FOR PERIOD ENDING NOVEMBER 30, 1966

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JULY 1967

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SUMMARY

Fluoride volatility processing at Oak Ridge National Laboratory is part of an intersite program to develop an alternative to aqueous methods for recovering valuable components that are present in spent UO_2 fuel from power reactors. Our main contribution will be the installation and operation of a pilot plant in several of the shielded cells in Building 3019.

Laboratory- and small-engineering-scale studies were made in support of the fluidized-bed volatility method for recovering low-enrichment UO_2 clad in Zircaloy-2. The volatility process proposed for these fuels uses a sequence of HCl to remove the Zircaloy cladding, oxidation of the exposed UO_2 with air to form U_3O_8 , fluorination with BrF_5 to form volatile UF_6 , and then treatment with fluorine to produce PuF_6 . All these steps and the pyrohydrolysis of ZrCl_4 to ZrO_2 are performed at elevated temperatures in fluidized alumina. The basic process was developed primarily at Argonne National Laboratory.

The design of the head-end portion of the pilot plant is well advanced, and many of the major head-end items of equipment are already fabricated. The installation of structural steel, shielding, and the process off-gas scrubber system is under way in cell 3. The design of the uranium product separation and purification equipment is continuing.

1. EXPERIMENTAL WORK

1.1 Organization and Facilities

Experiments were performed in three sections of the Chemical Technology Division and, under a subcontract, at the Columbus Laboratories of Battelle Memorial Institute. A 0.94-in.-ID fluidized-bed reactor was used in much of the laboratory-scale work. Other tests were made using a 1.5-in.-ID Pyrex unit and a 5/8-in.-ID rotating-bed reactor. Plutonium studies were made at two locations: the search for a sorption-desorption system for PuF_6 is being conducted in an alpha glove box in Building 3508; and LiF was evaluated as a sorbent for PuF_6 in Room 306, Building 3019.

Laboratory-scale equipment is being designed and fabricated for use in hot-cell tests of the fluidized-bed volatility process. A scrub column was developed to treat process off-gas from hot-cell equipment.

Small-scale engineering equipment is located in a test facility in Building 3503. The two fluidized-bed reactors located there are made of 2-in. and 4-in. sched 40 nickel pipe. A Plexiglas mockup of the primary reactor for the FBVPP was installed in Building 3019 for training and demonstration purposes.

1.2 Decladding and Oxidation

Three decladding-oxidation runs were made using the 2-in. reactor in the Unit Operations Section test facility. Fuel assemblies were simulated by loading 1-ft-long Zircaloy tubes with 3/8-in.-diam UO_2 pellets. In all three tests, trouble was experienced with operation of the pyrohydrolyzer bed during the decladding operation with either 40 or 60% HCl. Apparently, extreme spouting conditions existed in the bed because of increased gas velocity as a result of an increase in volumes of gas. Two failures of sintered nickel powder filters occurred in the pyrohydrolyzer off-gas stream at 400°C . During the period, an accidental contamination of the equipment from an external source of radioactivity interrupted studies for two months. Two tests with HF-O_2 as the decladding reagent for Zircaloy-clad fuels were made to determine the nature of the residue. In both tests relatively massive shards of ZrO_2 were produced.

In laboratory studies an alternative decladding and oxidation scheme was developed for UO_2 fuels clad in Zircaloy. It consists of (1) reacting the zirconium with hydrogen ("hydriding") to fracture the cladding, (2) converting the UO_2 to U_3O_8 by reaction with oxygen, (3) pulverizing the cladding by exposing it to HF-O_2 , and (4) fluorinating to volatilize the uranium and plutonium. Use of this method should eliminate difficulties now being experienced with filtering ZrCl_4 that is obtained from the HCl-zirconium reaction. Also, compared with the HF-O_2 process, the ratio of fuel charged to bed volume is about four times greater. The hydriding reaction proceeds very rapidly, making this method advantageous for thick

Zircaloy pieces. However, before the process could be seriously considered for large-scale application, process tests to study plutonium retention would be required.

Members of an MIT practice school team studied the size distribution of U_3O_8 particles formed by the oxidation of UO_2 pellets. Of the two distinct classes of U_3O_8 particles formed, the larger particles had a number-average diameter of 4.2μ , and the other class consisted of spherical particles with a number-average diameter of about 0.6μ . Filters made of sintered nickel fibers ($10\text{-}\mu$ rating) satisfactorily removed U_3O_8 from the exit gases from fluidized beds during tests.

1.3 Fluorination of Uranium

The fluorination step was studied, in the absence of plutonium, in both a 0.94-in.-ID fluidized-bed reactor and in a 5/8-in.-ID rotating-bed reactor. A statistically designed experiment was conducted to determine the effects of the following variables on the final uranium concentration in the alumina bed: temperature, fluorinating gas concentration and type, reaction time, and the initial concentration of uranium in the bed. In this experiment using the rotating-bed reactor, the change in the amount of uranium retained as a direct result of changing any of the five variables over the range studied was less than the experimental error. In other experiments using the rotating-bed reactor, some evidence was found that fluorine leaves less residual uranium than does BrF_5 , particularly at temperatures above $300^\circ C$. Treatment of the alumina with BrF_3 between the BrF_5 and the fluorine steps may be required to reduce the carry-over of uranium during the fluorination of plutonium with fluorine. In several experiments with a 0.94-in.-ID fluidized-bed reactor, BrF_3 was used successfully as a cleanup agent for the disengaging section, filter, and lines. After fluorination at $600^\circ C$, with either fluorine or BrF_3 , the final fluoride content of the alumina bed is twice that after fluorination at $500^\circ C$.

An experimental gas titrator was built and tested. It determines the concentration of bromine or BrF_3 in a gas stream by mixing fluorine with the stream and measuring the temperature rise. Such a device

should be able to measure as little as 5% utilization of BrF_6 in the off-gas from the fluidized-bed reactor, and thus provide an indirect measurement of the UF_6 concentration in the off-gas product stream.

1.4 UF_6 Purification

As an extension of earlier experiments to determine vapor-liquid equilibria of the UF_6 - NbF_5 system, the pressure-density-temperature relationships of the liquid and vapor phases of NbF_5 were determined.

1.5 Disposal of Fluorine and Bromine Fluorides

Apparatus for disposal of fluorine, bromine fluoride, and mixtures of these has been developed for use in forthcoming hot-cell experiments. Disposal is accomplished by allowing a 2 N KOH--0.2 N KI solution to flow concurrently with the gas through a vertical packed column. This method was designed to provide good fission product activity data for the off-gas streams from the processes tested. This apparatus has successfully disposed of 1500 ml (STP) of fluorine per minute without breakthrough.

1.6 PuF_6 Purification

The search for a solid sorbent to selectively and reversibly sorb PuF_6 continued to be concentrated on the use of LiF. The complex formed between PuF_6 and LiF was found to be similar to Li_4UF_8 by x-ray diffraction. Iodine titration techniques indicated that the plutonium in the complex had a valence of about 4. The chemical equilibrium was studied by the transpiration method and a relationship was determined between the fluorine: PuF_6 ratio in the gas and the temperature. The sorption and desorption characteristics of the LiF first used (prepared by fluorination of Li_2CO_3 at 400°C and having a surface area of 1 to $3 \text{ m}^2/\text{g}$) was distinctly different from that prepared later (by fluorination of Li_2CO_3 at 150°C and having a surface area of 25 to $35 \text{ m}^2/\text{g}$). The low-surface-area material sorbed PuF_6 well at 275 to 300°C but very poorly at lower temperatures, whereas the high-surface-area LiF sorbed PuF_6 well at 175°C . The PuF_6 could be desorbed almost completely from

the low-surface-area LiF at a rate that, except for a tailing-out effect with time, was in agreement with the chemical equilibrium.

With the high-surface-area LiF, the initial desorption rate was about as rapid as for the low-surface-area material; however, the final desorption rate was very slow, and apparently not all of the plutonium is desorbable.

The LiF sorption-desorption method was tested, using a 0.94-in.-ID fluidized-bed reactor and other laboratory-scale equipment that had been newly installed in a glove box in Room 306, Building 3019. Plutonium was fluorinated from fluidized beds of alumina as the hexafluoride, and the quantity sorbed by beds of LiF was related to the fluorine flow rate, the average $F_2:PuF_6$ mole ratio, the sorption bed temperature, and the surface area of the LiF. Early tests resulted in relatively poor retentions. When the surface area of the LiF was increased by a factor of about 6 ($9.1 \text{ m}^2/\text{g}$ compared with about $1.5 \text{ m}^2/\text{g}$), retentions of 96 to 97% of the plutonium were demonstrated at superficial velocities of 0.5 fps and average $F_2:PuF_6$ mole ratios of 3800:1. Higher efficiencies than these were concluded to be improbable at proposed sorption temperatures (about 250 to 350°C) because of the equilibrium constant, which was about 10^5 ($F_2:PuF_6$ mole ratio) over that temperature range. Sorption at temperatures below 250°C is currently being studied in an attempt to reduce losses to 1% or less.

1.7 Solids Sampling

The problem of obtaining a representative sample of solids from a fluidized bed was studied during the period. After oxidation of the UO_2 in the primary reactor to U_3O_8 , particle sizes are expected to range from greater than 300 μ to less than 1 μ in diameter. In a preliminary experiment 446 g of 325-mesh iron powder was mixed with 4600 g of -48 +100 mesh alumina. After 4.7 hr of fluidizing and sampling from an external sample circulating loop, approximately 20% of the iron present was elutriated and did not return to the bed. The remaining iron powder was moved toward the top of the fluidized bed.

The sampler consists of a gas jet and a venturi nozzle located in an external loop that circulates solids from the fluidized bed and then back to the vessel. When circulating of solids has been established, the flow can be stopped by operation of valves, and the entire contents of the valved-off section of the circulation line can be drained into a sample container. Experiments with such a system showed that -48 +100 mesh T-60 alumina could be adequately sampled. If reliable and consistent data on the particle size distribution of U_3O_8 can be obtained, elutriation correlations may allow a valid inventory analysis to be made directly from the fluidized bed.

1.8 Corrosion Studies

The study made at Battelle Memorial Institute - Columbus Laboratories to explain intergranular modifications of nickel exposed to fluidized-bed volatility process conditions was completed with the issuance of a summary report. Screening studies were continued at BMI to aid in choosing a constructional material for leaching equipment to be installed in the FBVPP. A leachant, 13 M HNO_3 --0.1 M HF , was used in laboratory corrosion studies. Results of ten-day tests indicate that Corronel 230 and Hanford Alloy 20 are still leading candidate materials for the leacher.

2. STATUS OF THE FLUIDIZED-BED VOLATILITY PILOT PLANT

2.1 Flowsheets

During the period the fluorination portion of the chemical flowsheet was changed. In the new procedure, BrF_5 will be used to volatilize the uranium and fluorine will be used to volatilize the plutonium, as hexafluorides. Batch distillation of the mixture of BrF_5 , UF_6 , and volatile fission products after cold trapping was also adopted as a purification method. The purification and recovery of plutonium are still being studied at ANL and, to a lesser extent, at ORNL. The target date for determination of a plutonium processing method is February 1967.

2.2 Equipment Design

The adoption of the interhalogen flowsheet required major changes in the layout of cell 3 and virtually a new approach in process piping. Two significant changes in the conceptual designs for the head-end equipment were made during the period. The primary and backup filters for both the primary reactor and the pyrohydrolyzer were combined into a single housing for each vessel. Thin-walled metal cans will be substituted for plastic bags for containing equipment while it is being transferred into and out of the cell.

2.3 Construction

Fabrication is complete for the process off-gas scrubber system, the $\text{BrF}_5\text{-UF}_6$ cold trap, and most of the head-end vessels.

Fabrication is virtually complete for the primary reactor and filter assembly, the pyrohydrolyzer, the fluorine compressor, the process off-gas scrubber system, and the $\text{BrF}_5\text{-UF}_6$ cold trap. Most of the gamma-shielding sections for cell 3 are fabricated. The process off-gas scrubber was installed and shielded; gamma shielding and alpha sealing for the reactor cubicle are about 80% complete at the first level, while less progress has been made at the higher levels.

All penetrations from cell 3 to other areas have been drilled. The process off-gas scrubber was installed and shielded, and curbing and floor sheathing have been completed in cell 3. Gamma shielding and alpha sealing for the reactor cubicle is under way.

The most recent schedule shows equipment and piping in cells 2 and 3 completely installed by August 26, 1968.

2.4 Criticality, Hazards, and Plutonium Handling

Work continues on the preparation of the hazards evaluation report. One significant area, from the standpoint of criticality, is the process off-gas scrubber. At present, we plan to use a soluble, rather than a fixed, poison for criticality control.

FLUORIDE VOLATILITY PROCESSING SEMIANNUAL PROGRESS REPORT
FOR PERIOD ENDING NOVEMBER 30, 1966

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G. I. Cathers

R. W. Horton
W. H. Carr

This report inaugurates semiannual reporting of work on fluoride volatility processing at Oak Ridge National Laboratory. The work has been, and will continue to be, reported in the Chemical Technology Division annual progress reports.¹ Fluoride volatility processing is an intersite program aimed at developing an alternative to aqueous methods for recovering valuable components that are present in spent UO_2 fuel from power reactors. The AEC's goals for this work, the responsibilities of other sites, and the possible advantages of volatility methods have been presented in earlier progress reports.

Currently, the fuel of most interest is low-enrichment UO_2 clad in Zircaloy-2. The volatility process proposed for these fuels consists in: (1) using HCl to remove the Zircaloy cladding and air to oxidize the exposed UO_2 to U_3O_8 , and (2) fluorinating, first with BrF_5 to form volatile UF_6 and then with fluorine to produce PuF_6 . These steps, as well as the pyrohydrolysis of ZrCl_4 to ZrO_2 are performed at elevated temperatures in fluidized alumina. The basic process was developed primarily at Argonne National Laboratory (with some early work at Brookhaven). Our main task is to design, install, and operate a "hot" pilot plant (Fluidized-Bed Volatility Pilot Plant - FBVPP) to demonstrate the process using actual spent fuel elements. Laboratory- and small-engineering-scale studies are also being conducted, principally for the following purposes: to directly support pilot plant design, to assist in the development of a PuF_6 purification step, to attempt to improve or better understand existing process steps, to improve the process applicability to stainless-steel-clad fuels, and, finally, to develop experience that will be helpful when operation of the pilot plant begins.

This report emphasizes the experimental effort and presents only a brief account of progress in the design and construction of the pilot plant.

The outline of the report, insofar as practicable, is based on the sequence of operations required in the process. The absence of the discussion of a particular step indicates that no work was done on that step during the reporting period.

1. EXPERIMENTAL WORK

1.1 Organization and Facilities

Experiments were performed in three sections of the Chemical Technology Division and, under a subcontract, at the Columbus Laboratories of Battelle Memorial Institute. Laboratory-scale studies were done in Chemical Development Section B under G. I. Cathers (R. E. Blanco, Section Chief); small-scale engineering studies were made in the Unit Operations Section and were directed by R. W. Horton (M. E. Whatley, Section Chief); and corrosion tests at BMI were the responsibility of R. P. Milford, who was assisted during this period by S. Mann, both of the Process Design Section (H. E. Goeller, Section Chief). The FBVPP will be operated under the supervision of W. H. Carr, Pilot Plant Section (R. E. Brooksbank, Section Chief). Some sampling tests were made in the Pilot Plant Section this period, using a clear-plastic mockup of the primary fluidized-bed reactor that has been fabricated for the FBVPP.

1.1.1 Laboratory-Scale Equipment

0.94-in.-ID Fluidized-Bed Reactor. - A 0.94-in.-ID fluidized-bed reactor (see Figs. 1 and 2) was designed and used for uranium and plutonium process tests. Figure 2 shows the pulsed blowback system used in most runs. Recently, a new blowback system (Fig. 3) was installed that uses a flow restriction in the off-gas lines instead of valves to direct a major part of the blowback gas flow through the filters; thus the problem of the sticking valves in the process gas lines has been eliminated. Two blowback filters are mounted in the disengaging section; each consists of a 1 x 4 x 0.080-in.-thick sheet of nickel Feltmetal,² 10- μ rating, which is welded into a filter tube. In the new blowback system, the filters are blown back by nitrogen pulses from pulse chambers that are

Fig. 1. View of the 0.94-in.-ID Fluidized-Bed Reactor, Including Disengaging Section and Blowback Filters.

N.O. = NORMALLY OPEN
N.C. = NORMALLY CLOSED

Fig. 2. Schematic Diagram of the 0.94-in.-ID Fluidized-Bed Reactor with Original Blowback System.

ORNL DWG 67-3636

Fig. 3. New Blowback System Used with 0.94-in.-ID Fluidized-Bed Reactor to Eliminate Valves in Process Line (cf. Fig. 2).

pressurized to about 20 psig. The Monel support ball prevents backup of the bed into the gas inlet tube. The 1-in. fluidized-bed section is heated to the reaction temperature in a furnace, and the disengaging section and filters are heated electrically to 150 to 300°C by using a coil of Nichrome wire. About 40 g of alumina and 35 g of UO_2 are used in a standard experiment. In plutonium runs, about 200 mg of PuO_2 is normally present.

1.5-in.-ID Pyrex Unit. - A 1.5-in.-ID Pyrex column with a 3-in.-ID disengaging section was used by an MIT Practice School team to study filtration of U_3O_8 powder. The lower section and the disengaging section were 8 and 10 in. high, respectively.

Rotating-Bed Reactor. - Small-scale uranium fluorination experiments were made in a 5/8-in.-ID, 3-1/4-in. long Inconel cylinder. This cylinder could be maintained at a temperature of at least 550°C by using a horizontal tube furnace. It was normally rotated at 3 rpm. The gas flow rate was usually 200 ml/min (STP), and the gas was fed directly into the rotating reactor through a 1/8-in.-OD nickel tube.

Equipment for Basic Sorption-Desorption of PuF_6 by Metal Fluorides. - The search for a sorption-desorption system for PuF_6 is being conducted in an alpha glove box in Building 3508. Principal components are quite small; the PuF_6 generator is 8 in. high and 3/16 in. in inner diameter, the test sorbent traps are either 2-1/2 in. high by 3/16 in. ID or 4 in. high by 7/16 in. ID, and the NaF backup trap is 2-1/2 in. high by 3/16 in. ID. These items are made of nickel, and connecting lines are of either copper or nickel.

PuF_6 Process Test Equipment. - The usefulness of LiF as a sorbent for PuF_6 was tested in Room 306, Building 3019. The process equipment was contained in a 6-ft-long glove box, and sample preparation was carried out in a small glove box (4 ft) adjacent to the larger box. An 8-in.-diam port connected the two boxes.

The fluidized-bed reactor was one of the 0.94-in.-ID nickel units described previously. Sorption beds consisted of 6-in. lengths of 1/2-in., 3/4-in., and 1-in.-OD nickel tubing wound with resistance wire and

insulation. Fluorine gas in the product streams was disposed of by reaction with a 50% mixture of soda-lime and activated alumina contained in an 18-in. length of 5-in.-OD brass tubing. For disposal, BrF_3 and HF were reacted with 2 N KOH . Also provided were a panelboard and the usual instrumentation: gas flow-rate indicators, differential pressure transmitters, control valves, and temperature recorders.

Scrubber for Hot-Cell Tests. - Laboratory-scale equipment is being designed and fabricated for use in hot-cell (cell 3, Building 4507) tests of the fluidized-bed volatility process. A scrub column was developed to dispose of bromine, fluorine, bromine fluorides, and mixtures of these. This column consists of a top section that is a 1-in.-OD, 1-ft-long Alundum tube and of a bottom section that is a 1-in.-OD by 2-ft-long stainless steel tube. The entire column is packed with fused alumina (4 mesh). An aqueous solution of 2 N KOH --0.2 N KI is the scrub liquid.

1.1.2 Small-Scale Engineering Equipment

Test Facility. - A small-scale engineering test facility, which is located in a cell in Building 3503, contains two fluidized-bed reactors (one made of 2-in., and the other of 4-in., sched 40 nickel pipe) and the necessary process equipment for decladding either Zircaloy- or stainless-steel-clad fuel with either HCl (for Zircaloy only) or HF-O_2 (for either metal). Oxidation and fluorination can also be done. The instrumentation and controls of this facility duplicate those to be used in the pilot plant as closely as possible, and all operations except fuel-element charging and process steps involving plutonium or fission products will be the same as in the pilot plant. The purpose of the facility is to test instrumentation and control equipment and to develop operating procedures.

Two glass columns, 2 in. and 4 in. in inner diameter, were used to test the effectiveness of sampling fluidized solids while they were circulating from the bed, through an external loop, and back to the bed.

Plexiglas Mockup of Primary Reactor. - A mockup of the primary reactor for the FBVPP was fabricated from Plexiglas and installed in

Building 3019 (Pilot Plant Section). The diameter of the mockup is the same as that of the 8-in.-ID primary reactor; however, the mockup is only 4 ft high and has no disengaging section. Its purpose was training and demonstration; tests of bed dumping and of sampling a fluidized bed were also made.

1.2 Decladding and Oxidation

1.2.1 Results of Decladding and Oxidation Tests with Zircaloy-Clad UO_2

R. S. Lowrie

W. W. Pitt

R. W. Horton

The experimental effort in this period was directed toward the decladding and oxidation of Zircaloy-clad UO_2 fuel. Fuel assemblies were simulated by loading 1-ft-long Zircaloy tubes (0.4 in. OD, 30-mil. wall thickness) with 3/8-in.-diam UO_2 pellets. Four tubes were arranged in a square array with tubes on 0.525-in. centers. The assembly was held together by two spacers made from 20-mil-thick stainless steel, each spacer being 1 in. from an end of the assembly.

Decladding with HCl. - Three decladding-oxidation runs were made using the 2-in. reactor. In the first two tests, 40% HCl was used for decladding; in the oxidation step, 33% oxygen--67% nitrogen was used first, followed by 100% oxygen. In the final run, 60% HCl was used, followed by an oxygen-nitrogen mixture that gradually increased in oxygen content from 10 to 100%. The $\text{UO}_2:\text{Al}_2\text{O}_3$ ratio was about 1:3.5 for these experiments (745 g of UO_2 , 2.6 kg of Al_2O_3), and the gas flow rates were set to give superficial gas velocities of 1 fps during hydrochlorination and 0.7 fps during oxidation. The run schedule called for a 2-hr decladding step at 400°C and a 2-hr oxidation step at 450°C.

In all three tests, trouble was experienced with operation of the pyrohydrolyzer bed during the decladding step. The unsteady flow may have been an indication of nonuniform fluidization. Both vibrating the bed and reducing (or stopping) the steam flow were helpful; in each case, the pyrohydrolyzer was filled with a fresh charge of the same type of alumina (-48 +100 mesh Alcoa T-60) that was used in the primary

reactor. Although the accumulation of ZrO_2 in the bed, as suggested by ANL, might modify the fluidizing behavior, we believe that extreme spouting conditions exist in the bed as a consequence of increase gas velocity, which, in turn, is the result of increased volumes of gas, as illustrated in the following sequence of reactions:

(1) primary reactor

Total moles of gas into reactor per mole of zirconium reacted	6.66
---	------

Total moles of gas leaving reactor per mole of zirconium reacted	5.66
--	------

(2) pyrohydrolyzer reactor

(assuming only stoichiometric addition of steam)

Minimum total moles of gas into reactor per mole of zirconium reacted	7.66
---	------

Minimum total moles of gas leaving pyrohydrolyzer per mole of zirconium reacted	8.66
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The effect is probably more noticeable in our 2-in.-ID reactor than it will be in the 8-in.-ID FBVPP reactor, but a good operating condition should be established in the pilot plant during "cold" runs.

Two failures of sintered nickel powder filters have occurred in the pyrohydrolyzer off-gas stream at 400°C as a consequence of the loss of bonding between the nickel particles. Presumably, this loss of bonding was caused by HCl corrosion, which resulted in cracking when the filters were blown back.

The second run in this series of three was interrupted by an accidental contamination of the equipment from an external source of radioactivity. The residue from the half-completed decladding run was left in the reactor for the two months required to decontaminate and rebuild

equipment. This could have caused filter damage, as well as internal corrosion of the vessel, that might have altered the wall effect on fluidization.

Decladding with HF-O₂. - Two tests using HF-O₂ as the decladding reagent for Zircaloy-clad fuel were made to determine the nature of the residue. In both runs, 40% HF--60% O₂ was used for 1 hr, and the composition of the gas mixture was then changed to 20% HF--80% O₂. The wall temperatures were held at 550°C for the entire run. When the HF concentration was reduced, an internal thermocouple showed a temperature increase of less than 100°C, and a slight amount of wall cooling was required.

The residues produced were relatively massive shards of ZrO₂, as previously described by workers at ANL and BNL. While these pieces were not detrimental to bed operation, their conversion to ZrF₄ might take an excessive amount of time because of the poor surface-to-volume ratio. The uranium compounds produced ranged in color from light gray through green to black; the dark pieces were the largest and might have contained some unchanged UO₂. One sample of oxidized pellets analyzed 13.5% U⁴⁺, 65.3% U⁶⁺, and 12.8% F, with oxygen not determined. The low U⁴⁺ content indicates a relatively small amount of UO₂.

1.2.2 New Decladding and Oxidation Method Using Hydrogen, Oxygen, and HF-O₂ in Sequence

J. C. Mailen

G. I. Cathers

The two current methods for processing Zircaloy-clad UO₂ have disadvantages. The best of these uses HCl to form volatile ZrCl₄. Recently, troublesome plugging of Feltmetal filters has occurred when ZrCl₄ is being filtered at about 300°C. The second process uses HF-O₂ mixtures to form ZrO₂ in the primary fluidized-bed reactor. Here the acceptable fuel load is quite small because of lumping of the UO₂ when it is constricted in the presence of HF-O₂ mixtures. We have estimated that the fuel-to-bed area ratio should not exceed 0.1.³ Since neither of these processes is ideal, alternative methods of processing have been investigated.

One such alternative method consists of reacting zirconium with dilute hydrogen ("hydriding") at about 600°C to fracture the cladding, oxidizing at about 450°C to disperse the UO_2 as U_3O_8 , completely pulverizing the cladding by treatment at 450°C with HF-O_2 mixtures, and fluorinating with fluorine at 450 to 550°C to volatilize the uranium and plutonium. The use of BrF_5 , BrF_3 , or ClF_3 at lower temperatures would also be feasible for removing the uranium. This method has been tested using a 0.94-in.-ID fluidized-bed reactor without difficulty. In one test, the fuel occupied about 43% of the cross-sectional area of the bed for a fuel charge about four times that possible with the HF-O_2 flowsheet.

The hydriding reaction proceeds readily at temperatures above 560°C in the presence of either solid fluorides such as NaF , LiF , or ZrF_4 , or a small amount of HF (added in the initial period). Of these possible "catalysts", ZrF_4 would be the obvious choice since it will be present if the bed is recycled. Recycled beds have been used in which the $\text{ZrF}_4:\text{Al}_2\text{O}_3$ ratio was 1:2. The hydriding reaction is exothermic, and effective penetration rates of 80 to 160 mils/hr are attainable. The density of the Zircaloy is reduced from 6.50 to about 5.65 g/cm³ after the reaction, and the hydrided material is severely cracked. These cracks allow penetration of oxygen in the second step such that the UO_2 is oxidized to a fine U_3O_8 powder. This oxidation step has only a slight physical effect on the zirconium hydride. The subsequent reaction of zirconium hydride with an HF-O_2 mixture is very vigorous and exothermic, but can be easily controlled by diluting the gas with nitrogen and by using only 5 to 10% HF in the mixture. The HF reacts with the fine U_3O_8 to form UF_4 . The final fluorination reaction is very smooth and requires only a relatively small amount of fluorine since the uranium is already converted to UF_4 . The presence of ZrF_4 in the bed does not result in losses of uranium greater than those observed with an alumina bed. In fact, in comparable 1-hr experiments using the rotating-bed reactor, where UF_4 was fluorinated from alumina and ZrF_4 beds by using fluorine at 542°C, the final uranium concentration in the alumina bed was 0.015% - about three times that in the ZrF_4 bed.

In summary, the proposed process has several advantages. It might eliminate filtration problems (at least those now being experienced with ZrCl_4) and, like the HF-O_2 process, it would only require a single reactor. In comparison with the HF-O_2 process, the ratio of fuel charge to bed volume, as previously mentioned, is about four times greater. The effective rate of the hydriding reaction for thick Zircaloy pieces, such as end plates and plugs, is distinctly favorable.

The possible disadvantages are those associated with the one-time usage of alumina and with plutonium retention. Presumably, greater volumes of high-level waste would result; however, if recycling of the alumina were feasible (i.e., if the alumina- ZrF_4 bed were reusable to the point where the bed was predominantly ZrF_4 , per se) this disadvantage would not exist.

The question of plutonium retention in a ZrF_4 bed has not been resolved. Experimental data concerning retention of plutonium by fluorides are incomplete and sometimes contradictory. Investigations at ANL⁴ yielded the following data when mixtures of inert solids and $\text{PuO}_2\text{-UO}_2$ were fluorinated at 450°C with 100% fluorine for 10 hr. These fluorinations were thin-layer boat tests.

<u>Inert Solid</u>	<u>Amount Retained by Solid Residue (%)</u>	
	<u>Uranium</u>	<u>Plutonium</u>
Al_2O_3	0.0007	0.027
ZrF_4	0.06	0.17

These results indicate that ZrF_4 retains too much plutonium. However, other available data contradict these results. At ORNL, 1-hr tests using both the 0.94-in.-ID fluidized bed and the rotating-bed reactor yielded uranium retentions by ZrF_4 of about 0.006 wt %. If the amount of plutonium retained is similarly reduced when the mixture is fluorinated in a fluidized bed, the retention of plutonium by ZrF_4 may be adequately low. The reason for the discrepancy in the experimental results is not certain, but it may be the result of the difference between boat and fluidized-bed tests. Boat tests are more dependent on particle size and would be highly dependent on the depth of the powder

layer. Boat tests usually give lower rates of volatilization than those found in fluidized-bed tests. Based on the available data, we cannot state whether ZrF_4 retains excessive plutonium or not. Before this process could be seriously considered, process tests to study plutonium retention would be required.

1.2.3 Filtration of U_3O_8 During Oxidation Step

J. C. Mailen H. F. Soard G. I. Cathers

During the oxidation step the UO_2 pellets are converted to a fine U_3O_8 powder. Photographic studies, using an electron microscope, revealed two distinct classes of U_3O_8 particles.⁵ The larger particles were irregular in shape, with a number-average diameter of about 4.2μ (Fig. 4). The mass-average diameter of this group is estimated to be about 6μ . The other class of particles consisted of spherical particles having a number-average diameter of about 0.6μ (Fig. 5). The mass-average diameter of this group is possibly 1.4μ . Work done by an MIT practice school team gives further evidence about the size distribution of the U_3O_8 particles.⁶ By using photomicrographs taken through an optical microscope at 1000X, sizes of more than 900 particles were measured with a Zeiss Particle Analyzer; a log-probability plot of distribution is shown in Fig. 6. Since this plot shows only the number of particles determined by optical methods, most of the spherical particles were not included because they were too small to be counted. However, the plotted data agree well with the earlier rough determinations of average diameter. Since most of the particles are less than 10μ in diameter, a distinct possibility exists that some of this U_3O_8 can pass through the process gas filters that are rated to remove 100% of all $10\text{-}\mu$ particles.

Experiments with a 0.94-in.-ID fluidized-bed reactor equipped with two filters, each with separate blowback pulsing (see Fig. 3), allowed approximately 1% of a U_3O_8 charge to pass through the filters during a 4- to 5-hr fluidization. Each of these filters consisted of a 1- by 4-in. flat piece of nickel Feltmetal, rated for 10μ , that was edge-welded into a holder. Some welding damage to the filters was found in

Fig. 4. Electron Photomicrograph of U_3O_8 Particles (High Particle Size Range). Formed in 2-hr fluidized-bed oxidation run at 525°C with 20° O_2 -80% He.

Fig. 5. Electron Photomicrograph of U_3O_8 Particles (Low Particle Size Range). Formed in 2-hr fluidized-bed oxidation run at 525°C with 20% O_2 -80% He.

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Fig. 6. U_3O_8 Particle Size Distribution.

tests that were conducted after the completion of the MIT filtration studies described below. Because of the magnitude of the U_3O_8 loss, an MIT practice team was assigned to study U_3O_8 filtration. Their data showed that the Feltmetal filters, when operated properly, are capable of filtering out essentially all the U_3O_8 . In fact, with a 1-1/2-in.-ID Pyrex column, a 3-in.-ID disengaging section and a 3-in.-diam filter, less than 0.0002% of the U_3O_8 passed through the filter in 4 hr of fluidization.⁶ The filter was mounted with a rubber gasket between two flanges. After receiving these results, we made further tests with the 0.94-in.-ID reactor. We then found that, if the filters were operated without blowback, loss of U_3O_8 did not occur. Further, no loss of U_3O_8 was obtained by either changing the temperature at which the UO_2 was oxidized from 450 to 525°C or by changing the temperature of the filter in the range of 50°C to 275°C in other tests. From these results we conclude that the losses experienced earlier can be attributed either to welding damage to the filters or to the alternating blowback system used.

Another interesting observation made during the experiment with the 1-1/2-in.-ID Pyrex fluidized-bed reactor was that the major portion (possibly more than 90%) of the U_3O_8 powder was suspended in the lower part of the disengaging section of the fluidizing gas. This indicates that much of the subsequent fluorination reaction will take place in the bottom part of the disengaging section. The superficial gas velocity in the disengaging section was one-fourth of that in the fluidization section.

The work with the Pyrex reactor also confirmed previous observations that, if the filter area for a particular set of operating conditions is above some minimum value, blowback is not required to prevent excessive back pressure. In the Pyrex reactor with blowback, the back pressure developed in one 1-hr oxidation run was excessive when the area of the filter was equal to the cross-sectional area of the bed, but it was low when the filter area was four times the bed area. In the 0.94-in.-ID reactor, the back pressure without blowback was excessive (greater than 10 psig) when the filter and reactor areas were equal, but was low

(less than 1 psig) when the filter-area:bed-area ratio was about 7. In the case of the Pyrex reactor, the filter was at the top of a 12-in.-high disengaging section; however, this did not prevent the development of back pressure in the case of the 1.5-in.-diam filter.

1.3 Fluorination of Uranium

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J. C. Mailen

After the oxidation of the fuel pellets, as discussed in the previous section, the uranium and plutonium will be volatilized from the fluidized bed and recovered as the hexafluorides. This will be done in two separate steps, with the uranium being recovered by treatment with BrF_5 and the plutonium being subsequently recovered by treatment with fluorine. This two-step process gives a clean separation of the uranium and plutonium. The fluorination step has been studied, in the absence of plutonium, using both a 0.94-in.-ID fluidized-bed reactor and a 5/8-in.-ID rotating-bed reactor. The results for the latter reactor were obtained by a summer participant.⁷ The rotating-bed reactor and its operation will be discussed first, and then its results and their significance with regard to the fluidized-bed reactor will be presented.

1.3.1 Effects of Five Process Variables on Retention of Uranium by Alumina After Treatment with Fluorine

A flow diagram of the rotating-bed reactor is shown in Fig. 7; this reactor is described in Sect. 1.1. Charges to the reactor weighed about 2-1/2 g, of which about 0.2 g was uranium as UF_4 . The flow rate of gas into the reactor was usually 200 ml/min (STP), sufficient to keep a nearly constant gas concentration in the reactor. The quantity of reacting uranium was insufficient to cause any significant variation in the temperature of the rotating reactor. Thus, the reactions could be studied at constant temperature in a constant-composition gas mixture. The tumbling action of the rotating bed was expected to approximate mixing in a fluidized bed.

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Fig. 7. Flow Diagram for Rotating-Bed Reactor Experiments.

Of interest in these experiments were the effects of the following variables on final uranium concentration: the particle diameter of the alumina (Norton RR grade), the fluorination temperature, the concentration of the fluorinating gas and type (whether fluorine, BrF_5 , or BrF_3), the time of reaction, and the initial concentration of uranium in the bed.

A statistically designed experiment⁸ was performed to evaluate the effects of these variables. A central composite design was used that consisted of the following 31 points: (1) 16 points comprising one-half of a 2^5 factorial (the base design), (2) ten axial points, and (3) five points all at the center of the design.

The intent of the experiment was to estimate a quadratic response surface in five variables and to find the values of these five variables that would minimize the response (i.e., percentage of uranium retained in the bed). The independent variables and their ranges were: diameter of the alumina particles in the bed, 68 to 274 μ ; fluorination temperature, 443 to 600°C; concentration of fluorine in the gas, 5 to 20 vol %; time of reaction, 37.5 to 120 min; and initial concentration of uranium in the bed, 0.1 to 3 wt % (the UF_4 consisted of particles about 112 μ in diameter). At flowsheet conditions, concentrations of uranium on the order of 40 wt % of the alumina bed are used; however, based on the observations in the Pyrex reactor used in studies of U_3O_8 filtration, the concentration of uranium in the fluidized bed at any time after the oxidation step will be much lower, perhaps within the range of concentration examined in these experiments. The conditions and responses for the 31 experiments are given in Table 1.

The data were analyzed by two individuals. One fitted⁹ the data to the model:

$$E(\ln y) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_5 + \beta_6 x_1 x_2 + \dots + \beta_{15} x_4 x_5 + \beta_{16} x_1^2 + \dots + \beta_{20} x_5^2$$

where

x_1 = diameter of Al_2O_3 particle,

x_2 = temperature,

x_3 = concentration of fluorine,

Table 1. Experimental Conditions and Results for Statistically Designed Study of Uranium Retention by Alumina

Design: Central Composite

Test No.	Independent Variables				Original Concentration of Uranium (wt %)	Response
	Diameter of Alumina Particles (μ)	Fluorination Temperature ($^{\circ}$ C)	Fluorine Concentration (vol %)	Fluorination Time (min)		Percentage of Uranium Retained
<u>Hypercube Points (minus half of 2^6 factorial)</u>						
1	194	542	20	92.5	0.825	0.0059
2	194	542	20	37.5	2.275	0.016
3	194	542	10	92.5	2.275	0.015
4	194	542	10	37.5	0.825	0.013
5	194	443	20	92.5	2.275	0.009
6	194	443	20	37.5	0.825	0.0043
7	194	443	10	92.5	0.825	0.00009
8	194	443	10	37.5	2.275	0.0003
9	96	542	20	92.5	2.275	0.008
10	96	542	20	37.5	0.825	0.006
11	96	542	10	92.5	0.825	0.010
12	96	542	10	37.5	2.275	0.008
13	96	443	20	92.5	0.825	0.023
14	96	443	20	37.5	2.275	0.012
15	96	443	10	92.5	2.275	0.015
16	96	443	10	37.5	0.825	0.014
<u>Axial Points</u>						
17	68	490	15	65	1.55	0.008
18	274	490	15	65	1.55	0.011
19	137	400	15	65	1.55	0.0099
20	137	600	15	65	1.55	0.020
21	137	490	5	65	1.55	0.020
22	137	490	25	65	1.55	0.0091
23	137	490	15	10	1.55	0.018
24	137	490	15	120	1.55	0.0082
25	137	490	15	65	0.1	0.0038
26	137	490	15	65	3.0	0.020
<u>Center Points</u>						
27	137	490	15	65	1.55	0.022
28	137	490	15	65	1.55	0.008
29	137	490	15	65	1.55	0.008
30	137	490	15	65	1.55	0.013
31	137	490	15	65	1.55	0.0094

x_4 = time,

x_5 = initial concentration of uranium.

The logarithmic transformation was used in an attempt to stabilize variances. The fit, however, was not "good". There was some doubt as to the adequacy of the model. The experimental error was large, as was evident from the wide range of responses obtained from the five experiments run at the center of the design. With this in mind, we obtained the values of the five independent variables that minimized $\ln y$, hoping that these values would be approximately those that minimized the true yield, y . These critical values are: diameter, 135 μ (intermediate between 100 and 120 U.S. sieve series); temperature, 491°C; fluorine concentration, 18 vol %; reaction time, 43 min; and initial uranium concentration, 1.32 wt %.

Unfortunately, a significant portion of the experimental data does not conform to the statistically derived equation since, at these low concentrations, sampling technique, cross contamination, and analytical variation become significant.

Results of the second analysis¹⁰ indicated that, based on the first 16 experiments, the change in the amount of uranium retained as a direct result of any of the five variables over the range studied is less than the experimental error. The data from these experiments seem to indicate a possible interaction between temperature and particle diameter; however, examination of data from other experiments not included in this series, as well as a more rigorous evaluation of the experiments mentioned above, failed to show such an interaction. Based on the data from the first 16 experiments and assuming no temperature-particle diameter interaction, the expected retention of uranium over the range of variables studied will be 0.010 wt %, with only one run in 40 expected to exceed 0.021 wt %.

1.3.2 Relative Effectiveness of Fluorine, BrF_5 , and BrF_3 in Minimizing Retention of Uranium by Alumina

In addition to the statistically designed experiment, the rotating-bed reactor was used to examine other problems, as discussed below.

If uranium and plutonium are to be volatilized separately with BrF_5 and fluorine, respectively, the quantity of uranium remaining in the bed after the BrF_5 step is of interest. If fluorine should volatilize some of this residual uranium in the subsequent step, then the plutonium stream will contain both uranium and plutonium, and further separation will be necessary. Experiments in which the rotating-bed reactor was used showed some evidence that fluorine leaves less residual uranium than BrF_5 . Figure 8 shows a plot of residual uranium vs temperature after a 65-min treatment with BrF_5 or fluorine; at all temperatures above 300°C , the fluorine left less residual uranium than did the BrF_5 . These data indicate that, if the BrF_5 treatment is followed by fluorine treatment in the pilot plant, the plutonium stream will contain some uranium. A possible solution is to treat the alumina with BrF_3 between the BrF_5 and the fluorine steps. Treatment of a bed with BrF_3 at 100°C gave a residual uranium content nearly as low as any value observed with fluorine at any temperature. These data, plus additional data on treatments with fluorine, BrF_5 , and mixtures of BrF_5 and BrF_3 are given in Table 2. Treatment with BrF_3 could also serve as a method for complete cleanup of the disengaging section, filters, and lines. In several experiments, using a 0.94-in.-ID fluidized-bed reactor, BrF_3 was used successfully in this respect. Some BrF_3 will be generated when BrF_5 is used for fluorinating, but this amount may not be sufficient for cleanup purposes.¹¹ Also, according to the results of the rotating-bed experiments, a mixture of BrF_5 and BrF_3 is not as effective at 100°C as BrF_3 alone.

Just as the residual uranium in the bed increases when the fluorination temperature is increased, the final fluoride content of the bed is higher at higher temperatures. This is shown in Fig. 9, where the final fluoride content after fluorination at 600°C is seen to be more than twice that after fluorination at 500°C . Minimizing the fluoride content of the discarded alumina could be important for subsequent disposal operations.

Fig. 8. Uranium Retained in Bed as a Function of Fluorination Temperature.

Table 2. Results Obtained by Fluorination of U_3O_8 in the Rotating-Bed Reactor

Rotary bed speed = 3 rpm

 U_3O_8 particle diameter = 200 to 300 μ

Average alumina particle diameter:

 BrF_5 runs = 194 μ BrF_5 - BrF_3 runs = 137 μ F_2 runs = 94 μ BrF_3 runs = 137 μ

Temperature (°C)	Time (min)	Fluorinating Agent			Initial U Conc. (%)	Final U Conc. (%)	Final F ⁻ Conc. ^a (%)
		F_2 (%)	BrF_5 (%)	BrF_3 (%)			
250	30	10	0	0	8.98	7.18	-
300	30	10	0	0	8.88	7.07	0.33
400	65	15	0	0	4.65	1.82	0.47
490	65	15	0	0	4.65	0.0021	0.67
600	65	15	0	0	4.65	0.025	2.55
100	30	0	10	0	0.9	8.18	-
200	30	0	10	0	8.9	7.59	-
250	30	0	10	0	8.2	4.87	-
300	30	0	10	0	8.9	0.70	-
200	65	0	15	0	4.65	1.72	0.27
100	30	0	22	25	4.48	0.621	0.09
100	60	0	22	25	4.65	0.434	0.09
100	30	0	0	15.8	4.65	0.0069	0.10
100	65	0	0	15.8	4.65	0.0037	0.10
50	30	0	0	2.6	4.66	4.13	0.10

^a $UF_4 + AlF_3$.

Fig. 9. Final Fluoride Content of Bed as a Function of Fluorination Temperature.

1.3.3 Gas Titrator for Determining Bromine and BrF_3 Contents of Primary Reactor Off-Gas

In the FBVPP, continuous measurements of the BrF_5 utilization during the uranium volatilization would be desirable, both to allow periodic addition of the proper amount of makeup fluorine to the off-gas stream and to determine when the reaction is complete. One possible way to provide such a measurement involves the use of a gas titrator, which is described below.

The gas titrator operates by reacting the exit gas stream, which consists of bromine, BrF_3 , and BrF_5 , with fluorine and measuring the increase in temperature. A schematic diagram of the titrator is shown in Fig. 10. The experimental model is about 6 in. long and 1/2 in. in diameter. It was wrapped with heating wire and heated to about 200°C . During operation, the heater voltage was maintained at a constant value. The simulated off-gas flowed through the titrator at about 1500 ml (STP)/min, and was mixed with fluorine near the middle of the titrator. Thermocouples upstream and about 3/4 in. downstream of the mixing point were connected to give a differential signal. The thermocouples were positioned in the wells shown in Fig. 10. In tests thus far, the quantity of fluorine supplied to the titrator has been exactly that required to react with the test mixture. Operating with a constant fluorine flow also is possible, and this would probably be the best mode of operation for a large-scale installation.

Figure 11 shows the calibration plots that were derived from testing the experimental titrator. Note that the calibrations give nearly straight lines and that bromine is much easier to detect than BrF_3 . When the titrator is operated with process off-gas, allowing the bromine and bromine fluorides to come to equilibrium before they enter the titrator will probably be desirable. This will prevent heat from being generated in the titrator when these gases react. If the gases are in chemical equilibrium, the amounts of bromine and BrF_3 present at any percentage utilization of the BrF_5 can be calculated. Then, if one assumes that the temperature rises generated in the titrator are additive, the response of the titrator vs percentage of BrF_5 utilized can be plotted as in

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Fig. 10. Schematic Diagram of Gas Titrator for Determining Bromine and BrF_3 Content of Gas Streams.

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Fig. 11. Experimental Calibration Plots for the Gas Titrator for Bromine and BrF_3 .

Fig. 12, where percentage utilization is based on conversion of BrF_5 to bromine. The plot shown is for an assumed inlet concentration of 10 vol % BrF_5 to the fluidized bed. Note that below 40% utilization, where no bromine is present in the off-gas, the response is not as great as it is above 40%. According to this plot, the titrator should be able to measure as little as 5% utilization.

In a large installation, such as the pilot plant, a fraction of the off-gas stream could be directed to the titrator. A possible method for control of the refluorination of the bromine and BrF_3 is illustrated in Fig. 13. The signal from the titrator would feed to a controller that, by comparing this signal with the calibration, would operate the makeup fluorine valve. Refluorination would take place in a reactor at a temperature of 200°C or higher.

1.4 UF_6 Purification

1.4.1 Estimation of Critical Constants for NbF_5

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R. W. Horton

As an extension of previously reported experiments to determine vapor-liquid equilibria of the UF_6 - NbF_5 system,^{1,2} the pressure-density-temperature relationships of the liquid and vapor phases of NbF_5 were determined. From these data the critical constants of NbF_5 were estimated using the Law of Rectilinear Diameters. This law states that the orthobaric densities are a linear function of temperature up to the critical temperature. The critical constants were estimated to be:

$$\rho_c = 1.21 \text{ g/cc,}$$

$$V_c = 0.155 \text{ liter/g-mole,}$$

$$T_c = 737^\circ\text{K,}$$

$$P_c = 62.0 \text{ atm.}$$

Fig. 12. Calculated Response of Gas Titrator to Off-Gas from Fluidized-Bed Reactor.

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Fig. 13. Diagram Showing Proposed Use of Gas Titrator in Pilot Plant.

1.5 Disposal of Fluorine and Bromine Fluorides

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G. I. Cathers

1.5.1 Advantages of Adding KI to Aqueous KOH

Hot-cell tests of the fluidized-bed volatility process are planned at ORNL, beginning about January 1967. One of the major problems has been the design of a compact system for the disposal of fluorine, bromine, bromine fluorides, and mixtures of these, which, at the same time, would permit analysis of the final solution to determine the amounts and kinds of fission product activities. The system resulting from these studies is described below.

We reported previously that a solution containing 2 M KOH and 0.2 M KI is very effective for the disposal of fluorine and bromine fluorides.¹¹ In earlier work at ANL the use of 0.01 M KI in KOH solution was also reported to increase the efficiency of fluorine absorption.¹³ Recently the fluorine and BrF₅ disposal apparatus shown in Fig. 14 has been built and tested. The column consists of a top section that is a 1-in.-OD by 1-ft-long Alundum tube and a bottom section that is a 1-in.-OD by 2-ft-long stainless steel tube. The entire column is packed with fused alumina (4 mesh). The Alundum top section and alumina packing were found to be necessary when previous models, which were constructed entirely of stainless steel, suffered excessive corrosion within the first 3 to 4 in. after the gas-liquid mixing point. Alundum shows very little, if any, corrosion under these conditions. A solution of 2 N KOH--0.2 N KI is fed into the top of the column and flows concurrently with the gas. On a volume basis, the flow rate of the liquid in the column is about one-tenth that of the fluorine. This apparatus has satisfactorily disposed of 1500 ml (STP) of fluorine per minute. The equipment has also been successfully tested with bromine fluorides and with mixtures of fluorine and BrF₅.

The beneficial effect of the KI was illustrated in two fluorine breakthrough tests, using 2 N KOH at a flow rate of 100 ml/min. With no KI present, breakthrough was detected at a fluorine flow rate of

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Fig. 14. Fluorine and BrF_5 Disposal Apparatus for Use in Hot-Cell Experiments.

100 ml/min; when the KOH solution was 0.1 N in KI, breakthrough was not detected until a fluorine flow rate of 600 ml/min was reached. (These experiments were done with a column only 18 in. long.)

A timer-operated solenoid valve at the bottom of the column will permit splitting of the effluent liquid stream for sampling. In the hot-cell tests, discarding most of the effluent to the hot drain will be advantageous.

The apparatus described has three major advantages with regard to the hot-cell work: its compactness, the ease of sampling for determination of the radioactivity that reaches it, and its usefulness for disposing of all gases that will be generated in the experiments.

1.6 PuF₆ Purification

1.6.1 Sorption of PuF₆ by Metal Fluorides and Its Subsequent Desorption Using Fluorine

S. Katz

G. I. Cathers

The volatility process might be improved by development of a sorption-desorption step that would separate PuF₆ from UF₆ and would then purify the PuF₆ from fission products. The separation step appears to be satisfied by the current BrF₅ flowsheet, but the problem of purifying PuF₆ remains. Over the past ten years, the sorbent NaF has been demonstrated to be satisfactory for the sorption-desorption purification of UF₆; however, no similar sorbent system has become known for PuF₆. A study, therefore, of possible sorbents for PuF₆ has been under way at ORNL since early 1965. Lithium fluoride has been selected as the most promising of the materials examined, and its characterization with respect to PuF₆ sorption-desorption is now in progress.

The selection of LiF as the most promising sorbent has been described in previous progress reports.^{14,16} Briefly, 31 possible metal fluorides representing all possible classes of candidate sorbents were exposed to PuF₆ in a static system; all except the fluorides of the groups I-A and II-A metals were eliminated from further consideration because only the

latter fluorides reacted with, or sorbed, significant amounts of PuF_6 . The fluorides of the I-A and II-A metals were then tested in 20-min sorptions from a fluorine stream containing PuF_6 . Temperatures were varied from 100 to 600°C. These tests showed that PuF_6 did not desorb rapidly from any of the candidate sorbents at a reasonable temperature. In longer tests (designed to examine possible slow desorption), no detectable desorption of PuF_6 was noted from NaF, even after 10 hr at 600°C; in separate tests, only 7 and 15% of the PuF_6 could be desorbed from CaF_2 in 10 hr at 600°C. With LiF, significant but slow desorption was noted at 400°C (about 9 hr to desorb 98%) and at 500°C (about 4 hr to desorb 98%). These rates are much larger than those reported for any other PuF_6 system. They permit consideration of LiF as a medium for a sorption-desorption system for PuF_6 , provided that the relatively slow desorption rate can be tolerated.

This section describes the equipment, materials, and the general methods being used in the study of LiF. The status of the study of the characteristics of the sorption process, the chemical equilibria, the desorption process, and the separation of PuF_6 and UF_6 are then presented. Finally, a brief discussion and plans for future work are presented.

Equipment, Materials, and Experimental Methods. - The principal components of the equipment (Fig. 15) are the PuF_6 generator, the LiF test trap, and the NaF backup trap; each is made of nickel. Connecting lines are of copper or nickel. The PuF_6 generator is 8 in. high and 3/16 in. ID with a 1/2-in. access on top. The LiF and NaF traps are each 2-1/2 in. high and 3/16 in. ID and hold either 1.7 g of LiF or 2.0 g of NaF, which rests upon a pad of nickel wire mesh forced into the trap bottom. A larger test trap, 4 in. high, 7/16 in. ID, and holding 7.8 g of LiF, was substituted as indicated. Temperatures were measured by thermocouples that were attached to the body of the PuF_6 generator and inserted into wells in the copper-block heaters used with the other traps; a correction for temperature differences was applied in the latter instances.

The NaF was -20 +40 mesh material that had been prepared from broken and screened 1/8-in. Harshaw pellets. The LiF was prepared by

ORNL DWG 66-8961 R2

A - NaF backup trap. Effective sorbent for PuF_6 from 100 to 600°C. 2 g of -20 +40 mesh material.

B - Test sorbent trap. Holds about 2 g of sorbent. In some cases two traps were used in series; in others, an 8-g bed was used.

C - For desorption tests, the fluorine bypassed the PuF_6 generator. Normal flow was 50 ml/min.

D - PuF_6 generator. PuO_2 or PuF_3 added before each test. Normal F_2 flow was 30 ml/min.

Fig. 15. System for Testing Sorption and Desorption Characteristics of Metal Fluorides for Use in PuF_6 Purification.

slow reaction of -20 +40 mesh Li_2CO_3 with dilute fluorine. The LiF prepared in this way at 400°C had a relatively low surface area (1 to $3 \text{ m}^2/\text{g}$) and is referred to as low-surface-area LiF. The LiF prepared at 150°C had a surface area of from 20 to $37 \text{ m}^2/\text{g}$ and is referred to as high-surface-area LiF. Intermediate-surface-area material resulted when LiF was prepared at temperatures higher and lower than 150°C .

In representative sorption experiments, the LiF and NaF traps were filled by pouring in premeasured volumes of sorbents. Ten to eighty milligrams of plutonium, either as dense PuO_2 or PuF_3 , was poured into the PuF_6 generator through the top access. After this access was closed, the temperature of each component was adjusted (PuF_6 generator, 600°C ; NaF trap, 200°C ; and LiF trap, desired test temperature), while the fluorine flow was set at 50 ml/min (STP) through a line bypassing the PuF_6 generator. Finally, the fluorine flow was diverted through the PuF_6 generator for 30 min. At the conclusion of the test the system was allowed to cool, and the materials from traps were poured into sample containers for determination of plutonium by alpha counting; the traps were reused. The sum of the plutonium found in the LiF and NaF traps was assumed to be the total that had reached the LiF trap during the test.

Prior to a desorption test, PuF_6 was sorbed upon the LiF, as described above, and the NaF trap was renewed. With the NaF trap at 200°C and the LiF trap at the desired test temperature, the fluorine flow was set at 50 ml/min (STP) and held there for the duration of the test, except for interruptions at intervals to renew the sorbent in the NaF trap. Sampling was similar to that for the sorption tests. The total plutonium content of the residual LiF and the NaF backup traps was assumed to have been originally held by the LiF.

Sorption of PuF_6 by LiF. - The parameters of gas flow rate, temperature, and surface area of LiF were studied, using the described procedure with the small LiF trap, which provides good sensitivity to variations in operating parameters. The chemical form of the sorbed plutonium was also studied. The loading of plutonium on the sorbent

was measured by using the larger (7.8 g) LiF trap and the low-surface-area LiF.

Effects of gas flow rate, temperature, and surface area of LiF are illustrated by the data shown in Table 3. Results for a variety of flow and temperature conditions for the low-surface-area LiF and for a single flow rate for the high-surface-area LiF demonstrate that sorption is only slightly affected by gas flow rates below 60 ml/min and that the effect at 250 ml/min is not large. For the low-surface-area LiF, a temperature of 300°C is required to achieve a PuF_6 retention comparable to that achieved with high-surface-area LiF at 175°C. Furthermore, partial sorption occurs at temperatures of 35 to 175°C in the case of the high-surface-area LiF, in contrast to almost no sorption at temperatures up to 200°C for the low-surface-area LiF.

The plutonium that is sorbed by low-surface-area LiF at 300°C has previously been shown to be tetravalent by the iodine liberation method. Also, the x-ray pattern is similar in most respects to that of Li_4UF_8 . The plutonium that was sorbed at 175 and 100°C by high-surface-area LiF was found by the iodine liberation method to have an average valence of 4.21 and 4.55 respectively.

The sorptions to determine the loading of plutonium on LiF were similar to those described previously in the subsection, "Equipment, Materials, and Experimental Conditions" [gas flow rate - 50 ml/min (STP)], except that 15 separate sorptions were cumulatively made on a single 7.8-g batch of low-surface-area LiF at 300°C. For each of the 15 sorptions, about 50 mg of plutonium as PuO_2 was added to the PuF_6 generator, and the NaF backup trap was renewed. A total of 0.76 g of plutonium as PuF_6 was passed into the sorbent bed (Fig. 16); 0.71 g was retained. The plutonium on the LiF sorbent at the end of the test varied from 0.1225 g of plutonium per gram of LiF near the entrance to 0.0309 g per gram of LiF at the exit.

Chemical Equilibrium in the Sorption-Desorption System. - The transpiration method was used to measure the equilibrium between PuF_6 , fluorine, and the sorbed plutonium complex (probably Li_4PuF_8). About

Table 3. Effects of Gas Flow Rate, Temperature, and LiF Surface Area on PuF_6 Sorption

Temperature of LiF (°C)	Percentage of Original Plutonium Retained by				
	Low-Surface-Area LiF				High-Surface-Area LiF
	At Gas Flow Rate (ml/min) ^a				At Gas Flow Rate (ml/min) ^a
	10	30	60	250	50
35					95.2
75					71.2
125					98.6
150					91.8
					99.9
					99.0
175					98.9
					98.1
					97.8
					99.8
					99.6
					99.3
200		24.7			98.2
250		73.6		60.7	
255	87.2				
265	89.3				
275				56.8	
280	98.4	95.6	97.2		
		93.5			
300		99.5		88.8	99.9
		99.5			
		99.8			
		99.5			
		99.3			
		99.7			
		94.0			
		99.9			
320	97.3				

^aSTP.

TOTAL OF 760 mg OF Pu WAS PASSED INTO THE 7.8-g BED OF LiF AT 300°C IN ~50-mg INCREMENTS
(710 mg or 93.4% Retained).

Fig. 16. Capacity of LiF for Sorbing PuF_6 .

300 mg of plutonium was first sorbed by a 7.8-g bed of low-surface-area LiF using the described sorption procedure, except that the temperature of the PuF_6 generator and the LiF sorbent bed were the same (in one instance, 400; in the other, 500°C). Use of the same temperature for the generator and the sorbent bed reduced the possibility that thermal decomposition would result in deposition of PuF_4 in the sorbent bed.

These data are plotted in Fig. 17 and fit the relationship

$$\log K = 2047/T(^{\circ}\text{K}) + 0.827,$$

where K = fluorine: PuF_6 mole ratio. At convenient temperature increments, the K values are:

<u>Temperature ($^{\circ}\text{C}$)</u>	<u>K</u>
100	2.01×10^6
200	1.40×10^5
300	2.45×10^4
400	7.25×10^3
500	2.92×10^3
600	1.45×10^3

The free energy change for the reaction

appears to be $F = 9360 + 3.74 T(^{\circ}\text{K})$ cal/mole.

The assumption necessary for the transpiration method to be applied is that equilibrium is reached in the residence time used; in each series the residence time was varied by a factor of 2, with no noticeable variation in results.

Desorption of PuF_6 from LiF. - A series of desorption tests (Table 4) with low-surface-area LiF gave results consistent with the equilibrium data presented in the previous section. The desorption rate increases with temperature up to approximately 550°C; here, the relationship reverses, possibly as a result of sintering. The desorption rate decreases with respect to time, causing a tailing-out effect. At the low flow of 2 ml (STP) of fluorine per minute, the initial desorption was very low

Fig. 17. Equilibrium Between Fluorine and PuF₆ in the Presence of LiF and Sorbed Plutonium Fluoride--LiF Complex.

Table 4. Desorption from Low-Surface-Area LiF
Using Small (3/16-in.-ID) Test Traps

Temperature (°C)	Fluorine Flow Rate (ml/min) ^a	Results
410	30	Total of 83.5 mg of plutonium desorbed in ten 1-hr desorptions: approximately 8, 11, 9, 7, 8, 9.5, 10, 9, 7, and 5 mg respectively; 4.5 mg left on bed.
425	2	Total of 44.5 mg of plutonium desorbed in four 6- to 7-hr desorptions: 8, 34, 0.3, and 2.2 mg respectively; 1 mg left on bed.
450	30	Total of 42.0 mg of plutonium was desorbed in six 1-hr desorptions: approximately 9.6, 10.3, 11.6, 9.3, 1.0, and 0.2 mg respectively; 1.5 mg left on bed.
475	30	Total of 80.0 mg of plutonium desorbed in six 1-hr and one 3-hr desorptions: 19, 14.9, 16.3, 17, 10.8, 1.3, and 0.7 mg respectively.
500	30	Total of 59.0 mg of plutonium desorbed in five 1-hr desorptions: 22, 20, 12, 3, and 2 mg respectively; 1.3 mg left on bed.
550	30	No desorption noted in 1 hr.
600	30	Only 8 mg desorbed in 1 hr.

^aSTP.

but then became comparable to that in other tests. This indicates that an induction reaction may be occurring and that diffusion to the solid surface may be a rate-determining step.

In a series of five cycles of sorption-desorptions using the low-surface-area LiF (Table 5), the quantity of residual plutonium on the LiF did not increase from that noted for one cycle.

In desorption from high-surface-area LiF (Table 6), the initial desorption appears comparable to that found with low-surface-area LiF.

Table 5. Five PuF_6 Sorption-Desorption Cycles on Low-Surface-Area LiF

Sorption conditions: LiF at 300°C ; fluorine flow rate of 30 ml/min (STP) for 30 min.

Desorption conditions: LiF at 450°C ; fluorine flow rate of 30 ml/min for 150 min.

Cycle	Amount Plutonium Desorbed ^a (mg)
1	23.4
2	45.5
3	41.5
4	43.3
5	37.3

^aResidual plutonium on LiF: 10.4 mg of plutonium remained on the LiF after the five cycles. Of this amount, 9.4 mg was desorbed in 13.5 hr at 450°C and a fluorine flow rate of 30 ml/min. One milligram of plutonium was left on the final sorbent bed.

Table 6. Desorption From High-Surface-Area LiF
Fluorine flows of 50 ml/min (STP) from small test traps

Desorption Temperatures (°C)	Results
475	Total of 77.9 mg of plutonium desorbed in one 4-hr and seven 7-hr desorptions at 475°C; 61.3, 6.0, 3.2, 2.7, 1.9, 1.2, 1.1, and 0.5 mg respectively; 4.1 mg left on bed.
350 for 2-1/4 hr 475 for 2-1/4 hr 475 for 4 hr 475 for 5 hr 475 for 7 hr 475 for 6-1/2 hr 475 for 5 hr	Total of 13.2 mg of plutonium desorbed in one period at 350°C followed by 6 periods at 475°C: 0.2, 1.3, 2.9, 3.3, 2.7, 1.7, and 1.1 mg respectively; 0.5 mg left on bed.
330 for 3 hr 380 for 6-1/2 hr 425 for 6 hr	Total of 26.4 mg of plutonium desorbed in three periods of increasing temperatures: 5.0 mg at 330°C, 12.5 mg at 380°C, and 8.9 mg at 425°C; 2.7 mg left on bed.

However, the tailing-out effect appears extended and, at least at the relatively high desorption temperature of 475°C, not all the plutonium appears desorbable. This condition results from sintering of the sorbent, which is evidenced by the significant reduction of the surface areas to about 3 m²/g.

Separation of Plutonium and Uranium. - The separation of plutonium and uranium hexafluorides was demonstrated in duplicate sorption tests in which both PuF₆ and UF₆ were produced in the PuF₆ generator and two LiF traps filled with low-surface-area LiF at 300°C were substituted for the single LiF trap as in the described procedure. No uranium was detected in the LiF traps, while 4.9 and 17.6 mg were found in the NaF

traps. In the first test, the two LiF traps and the NaF trap contained 61.4, 3.0, and 0.3 mg of plutonium respectively; in the second test, corresponding values were 61.9, 4.5, and 0.4 mg of plutonium.

Discussion and Future Work. - Results of this study to date indicate that the form of LiF to be used in the FBVPP will depend on the process flowsheet. If low excesses of fluorine are employed, a low-surface-area LiF may be preferred because it is stable, sorbs well from low fluorine excesses, separates PuF_6 from UF_6 , permits essentially complete desorption of the PuF_6 , and can be recycled. If high fluorine excesses are employed, a high-surface-area LiF may be preferred since more complete sorption is achieved with it than with the low-surface-area LiF. However, separation of PuF_6 from UF_6 has not yet been demonstrated for this material; complete desorption of the PuF_6 may be a problem, and the sorbent could not be recycled.

Additional work is planned on the problems noted above. The effect of other process impurities will then be evaluated.

1.6.2 Tests of PuF_6 Sorption by LiF, Using a Fluidized-Bed Reactor

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To test the proposed LiF sorption-desorption method for collecting and purifying PuF_6 , laboratory-scale equipment in which plutonium could be handled was installed in a glove box in Room 306, Building 3019. The experiments reported in this section were made using a 0.94-in.-ID fluidized-bed reactor and were confined, essentially, to the evaluation of PuF_6 sorption by LiF. In the tests, plutonium was fluorinated from fluidized beds of alumina as the hexafluoride, and the quantity sorbed by beds of LiF was determined with respect to such variables as fluorine flow rate, average $\text{F}_2:\text{PuF}_6$ mole ratio, sorption bed temperature, and surface area of the LiF.

Early tests, using low-surface-area LiF, resulted in relatively poor retentions; however, when the surface area of the LiF was increased by a factor of about 6 ($9.1 \text{ m}^2/\text{g}$ compared with about $1.5 \text{ m}^2/\text{g}$), plutonium retentions of 96 to 97% were demonstrated at superficial

fluidizing velocities of 0.5 fps and average F_2 : PuF_6 mole ratios of 3800:1.

Higher efficiencies than these were concluded to be improbable at proposed sorption temperatures (about 250 to 350°C) because of the equilibrium constant of about 10^5 (F_2 : PuF_6 mole ratio) over that temperature range. Sorption at temperatures below 250°C is currently being studied in an attempt to reduce losses to 1% or less.

Equipment. - The 0.94-in.-ID fluidized-bed reactor used in these tests is described on page 9. Other equipment and gas disposal methods are described on page 14. Figure 18 is a photograph of the glove-box installation.

Preliminary tests. - Duplicate tests using simulated process flow-sheet conditions were made to determine material balances and deposition profiles for plutonium in the disengagement section and filters of the reactor vessel. In each test, a 14-g mixture of 5% PuO_2 -- UO_2 was fluorinated from a 40-g bed of alumina (Norton RR; -90 +100 mesh) for 4 hr at 550°C and a gas fluidization velocity of 0.55 fps [1200 ml/min (STP)]. The products, gaseous PuF_6 and UF_6 , were then trapped on appropriate beds of NaF. Plutonium deposited on the filters and walls of the disengagement section was recovered by washing with dilute HNO_3 and accounted for about 1 to 2% of the total plutonium inventory in each test. The extent of deposition demonstrated in these tests makes it evident that the disengagement section will have to be maintained at least at the minimum fluorination temperature for the F_2 - PuF_4 reaction. Satisfactory corresponding material balances were obtained: 100.2% in one test, and 84.5% in the other.

Sorption by LiF at 300°C. - Process flowsheet conditions were used in the first test in a series of experiments designed to evaluate the sorption of PuF_6 by LiF. The charge was 7.0 g of 5.5% PuO_2 -- UO_2 (sol-gel-derived microspheres with diameters between 300 and 450 μ) contained in 4 g of type 304 stainless steel cladding. The simulated fuel was placed in a 40-g bed of 90- to 100-mesh Norton RR alumina. Oxidation was achieved at 600°C with a 20:80 vol % mixture of HF - O_2 for 30 min,

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Fig. 18. View of Glove-Box Installation for Plutonium Process Studies.

followed by a 40:60 vol % mixture for 1 hr. The residue was then treated with fluorine for 4 hr at 550°C at a gas fluidization velocity of 0.55 fps [1200 ml/min (STP)]. The product gas stream, consisting of PuF_6 - UF_6 - F_2 and some CrO_2F_2 - CrF_6 , was then passed through two 25-g beds of LiF (-12 +20 mesh) in series at 300°C. The LiF was the low-surface-area material (1.5 to 3.4 m²/g) described in the preceding section. A 10-g bed of NaF at 350°C was located downstream of the LiF sorption beds as a backup trap for any unsorbed PuF_6 . The average F_2 : PuF_6 mole ratio in the test was 5700:1. Of the 331 mg of plutonium volatilized as PuF_6 , 13 mg (3.9%) was sorbed by the first 25-g bed of LiF and 9 mg (2.9%) was sorbed by the second 25-g bed, giving an overall sorption of about 7%. The remaining 309 mg (93%) was accounted for in the NaF backup trap. Analysis of the LiF for chromium accounted for 83% of the total amount volatilized (1.15 g as CrF_6); however, the effect of this on the co-sorption of PuF_6 is not known. A second test was made in which chromium was eliminated from the product stream by omission of the stainless steel decladding cycle. Using a 7.0-g charge of PuO_2 - UO_2 as in the previous run, a 3-hr fluorination was carried out at 550°C and 0.55 fps. Of the 282 mg of plutonium volatilized, 59 mg (20.8%) and 37 mg (13.1%) were sorbed by the first and second 25-g beds of LiF respectively, giving a total sorption of 34%. The average F_2 : PuF_6 mole ratio in this test was 3800:1, and the plutonium balance was 93.5%. The greater retention of PuF_6 on the LiF (34% vs 7% in the previous test) was first thought to have been attributable to the lower F_2 : PuF_6 mole ratio (3800:1 vs 5700:1). Recent studies relating to the LiF used in sorption tests, however, have disclosed significant variances in surface area among batches prepared under similar conditions. For example, surface areas of LiF batches prepared from fused Li_2CO_3 by reaction with fluorine at 400°C have ranged from 1.3 to 3.4 m²/g, at 200°C from 5.9 to 17.7 m²/g, at 250°C from 6.5 to 36.8 m²/g, and at 100°C from 3.5 to 9.1 m²/g. Since it was further demonstrated that surface area has an appreciable effect on the sorption rate of PuF_6 , the importance of variables such as F_2 : PuF_6 ratios and absence of chromium, previously mentioned, is subject to some uncertainty.

Sorption by LiF at 250°C. - Based on the results of tests conducted by S. Katz, in which sorption efficiencies of PuF_6 on LiF were determined with respect to temperature, a change in bed temperature (from 300 to 250°C) was recommended. Using conditions identical to the previous test, but with the LiF bed temperature at 250°C instead of 300°C, a 3-hr fluorination was carried out. Of the 336 mg of plutonium volatilized, 108 mg (32.2%) was sorbed on the first 25-g bed of LiF and 80.5 mg (23.8%) was sorbed on the second 25-g bed, giving an overall sorption of 56%. This was an improvement over the 34% sorption achieved in the 300°C LiF bed test; however, it was still not sufficiently high to meet process requirements.

Sorption by Four Beds of LiF at 350°C. - The kinetics of the sorption was investigated by means of a test in which the LiF bed temperature was increased from 250 to 350°C. In this test, a 3-hr fluorination was used as before; however, the amount of LiF was doubled to give four 25-g beds in series at 350°C. A 10-g backup trap of NaF was placed downstream to collect any unsorbed PuF_6 . Of the 289 mg of plutonium volatilized, a total of 233 mg (81%) was sorbed over the four beds. Some intermixing of the material in adjacent beds occurred during disassembly of the equipment; however, from lithium and plutonium analyses, the corrected sorptions per 25-g section were 25, 22, 16, and 18%, respectively, of the total plutonium volatilized. The estimate of 47% sorption on the first 50 g of LiF, again, was not appreciably different from that obtained in either of the previous tests, where retentions were 34 and 56%.

Sorption at Increased Residence Times and Effect of F_2 : PuF_6 Mole Ratio. - In a static bed test in which the residence time for PuF_6 in the LiF bed was increased fivefold by fluorinating at a subfluidization velocity of 0.1 fps [240 ml/min (STP)] for 3 hr at 550°C, an overall sorption of 99.4% was achieved on a 50-g bed of LiF at 300°C. Of the initial 308 mg of plutonium, only 152.3 mg reached the sorption bed; however, of the latter amount, 132 mg was sorbed on the first 25-g bed and 19.7 on the second 25 g. The amount of plutonium passing through the bed and collected in the NaF trap was 0.6 mg; 25.9 mg was left in the reactor. The low material balance (57.8%) and the correspondingly

high LiF sorption (99.4%) achieved suggested that thermal decomposition may have occurred both in the cooler product off-gas lines and in the LiF bed. The $F_2:PuF_6$ mole ratio below which thermal decomposition of PuF_6 occurs has been reported to be 396:1 at 300°C.¹⁶ In this test, the mole ratio was 1270:1, based on a continuous evolution of plutonium over the 3-hr period. It was necessary, therefore, to determine the actual mole ratio. This was effected by making a duplicate test in which a neutron counting tube was positioned adjacent to the LiF sorption bed and calibrated with a known amount of plutonium (see Fig. 19).

Fluorination was then accomplished as in the previous test. During the first 25 min, the neutron count remained relatively constant at a background of about 960 counts/min. Over the next 5-min period, the rate increased to 1260 counts/min, where it remained for an additional 25 min. At this point, the rate became constant at about 1950 counts/min. A comparison with the neutron calibration value indicated that the amount of plutonium in the bed at this time was about 50 to 60% of the initial charge, correspondingly closely to the analysis value of 45.2%. On this basis, the actual $F_2:PuF_6$ mole ratio during the fluorination in both tests dropped below the required value of 396:1. The low ratios support the previous conclusion that thermal decomposition of PuF_6 was a contributing factor to the low material balance and the high sorption.

In another test, the extent of PuF_6 transfer through the LiF bed at the proposed sorption temperature of 300°C was determined by fluorinating PuF_6 onto a 50-g bed of LiF (-12 +20 mesh) at that temperature and continuing the fluorination for a 12-hr period at a rate of 240 ml/min (STP). At that time, 3.4 mg of plutonium (2.4% of the sorbed plutonium) had been transferred from the LiF and collected in a 10-g backup trap of NaF at 300°C. The average $F_2:PuF_6$ mole ratio in the exit stream of the LiF bed was about $5 \times 10^5:1$.

Sorption by Higher-Surface-Area LiF at 250°C. - It was reported at this time that an increase in the surface area of LiF that was normally prepared from fused Li_2CO_3 by fluorination at 400°C could be achieved by reducing the fluorination temperature. In a test with LiF having a surface area of 9.1 m²/g, higher by about a factor of 6 than any previously

Fig. 19. Determination of Actual Fluorine: PuF_6 Mole Ratios by Neutron Counting (α -n Reaction) Method.

used, a PuF_6 sorption of 96.1% was achieved under process flow conditions. In this test, plutonium was volatilized from a 40-g bed of alumina for 3 hr at a temperature of 550°C and a flow rate (0.5 fps) of 1200 ml/min (STP). The product gas stream was then passed through two 25-g beds of the specified LiF in series at 250°C . Of the 284.5 mg of plutonium reaching the beds, 269 mg, 4.5 mg, and 11.0 mg were sorbed, respectively, on the first 25-g bed, the second 25-g bed, and the NaF backup trap. The amount of unsorbed PuF_6 corresponded to a value for the equilibrium constant of about 10^5 ($\text{F}_2:\text{PuF}_6$ mole ratio), which is in close agreement with a value of 6×10^4 obtained in a previous study by S. Katz.

Conclusions. — The data from all of the tests reported here are summarized in Table 7. The 4% loss in the last test would still not be satisfactory for process use without recycling of the product stream. Recent studies, however, seem to indicate that PuF_6 sorption by LiF can be achieved at temperatures below 250°C (possibly as low as 150°C), where the equilibrium value would be more favorable and recycling would be unnecessary.

Table 7. Summary of PuF_6 on LiF

Average Mole Ratio ($\text{F}_2:\text{PuF}_6$)	LiF (-12 +20 mesh)		Sorption Temperature ($^\circ\text{C}$)	Sorption (%)	Material Balance (%)
	Wt (g)	Surface Area (m^2/g)			
5700	50	1.5 - 3.4	300	7	106
3800	50	1.5 - 3.4	300	34	93
5700	50 ^a	1.5 - 3.4	350	47	92
5700	50	1.5 - 3.4	250	54	107
1270	50	1.5 - 3.4	300	99.6	58
1270	50	1.5 - 3.4	250	97.6	51
5700	50	9.1	250	96.1	105

^aCorrected to first 50 g of bed.

Future Work. - Studies now in progress in the plutonium facility include investigation of the chemical reduction of PuF_6 to PuF_4 in the product gas stream using bromine gas, and separation and recovery of PuF_4 from the $\text{PuF}_4 \cdot x\text{NaF}$ complex by dissolution in anhydrous HF or BrF_3 . The product, insoluble PuF_4 , would then be separated from the dissolved NaF by filtration or by a settling-decantation procedure followed by evaporation of any excess liquid remaining with the PuF_4 product.

1.7 Solids Sampling

R. S. Lowrie

R. W. Horton

1.7.1 Sampling from a Fluidized Bed Using an External Circulation Loop

The processing efficiency of any type of chemical plant is normally calculated from a material balance derived from the input and output of each chemical species. For plants processing nuclear reactor fuels, these data are needed to account for fissionable material for safety reasons as well as for the usual economic evaluation.

In a dry process, such as fluidized-bed volatility, a truly homogeneous sample of input can never be obtained, and only one of several output streams (i.e., the decontaminated UF_6 product) can be easily sampled. All other outputs from the process will be in the form of heterogeneous particulates or mixed gases. The gases will be monitored but probably will not contribute any significant data to the material balance on fissile and fertile materials. The development effort must be concentrated on obtaining consistent data from batches of heterogeneous solids in various items of process equipment. Some of these items will be small sorption traps that will parallel larger traps and will receive a known fraction of the process gas flow; solids from these small traps will be dissolved to obtain a homogeneous sample. The two major batches of solids to be sampled are the fluidized bed before and after each product has been volatilized.

Prefluorination Sampling. - In the process, the fuel element will be charged into the fluidized bed, the Zircaloy containment tubes will

be treated with HCl, and the volatile ZrCl_4 will be swept out of the system. The remaining bed of UO_2 pellets (containing fission products and transuranium products) will be oxidized in the fluidized bed of alumina to simultaneously convert the uranium to U_3O_8 and reduce the UO_2 pellets to much finer particles. The opportune time to sample the process batch for input data would be after oxidation. According to the current flowsheet, the primary reactor will contain 58 kg of alumina ranging in size from 300 to 150 μ (-48 +100 mesh). After oxidation it will contain, in addition, about 38 kg of U_3O_8 . The particle size distribution of this material is not yet entirely predictable; however, in our experiments, it has ranged from greater than 300 μ to less than 1 μ in diameter. When beds containing such a broad range of particle sizes are fluidized, the finest particles are elutriated. The amount of fine U_3O_8 that will leave the fluidized bed is of major interest, both in sampling and in process operations.

In a preliminary experiment 446 g of 325-mesh iron powder was mixed with 4600 g of -48 +100 mesh T-61 alumina. After 4.7 hr of fluidizing and sampling from an external sample-circulating loop (see Fig. 20), the system was emptied and the distribution of solids in various parts of the system was determined (see Table 8). Data from similar experiments indicate that generally about 20% of the iron is elutriated. The iron remaining in the bed was not uniformly distributed; at the end of the test, the bottom section appeared white (containing only alumina), while the top layer was very dark.

Since the same process of elutriation will apply when U_3O_8 particles are present in the bed, a sample taken at any single point cannot be used to estimate the total uranium content of the bed; the purpose of sampling, as now conceived, is to provide a means of determining the plutonium: uranium ratio. If this ratio can be determined from the solid sample after oxidation, then the weight of uranium product can be found from weighing and sampling the cold trap, and, subsequently, the plutonium charge can be computed.

Experiments with a gas-jet-powered sampler connected to fluidized beds operating in 2-in. and 4-in. glass pipe columns have shown that

ORNL DWG 67-1486

Fig. 20. Sample-Circulating Loop for Fluidized-Bed Reactor.

Table 8. Distribution of Iron Powder in 2-in. Fluidized-Bed Glass Column

Fluidized with dry air at a superficial velocity of 0.7 fps for 4.7 hr

Alumina: 4.6 kg of Alcoa T-61, -48 +100 mesh

Temperature: ~25°C

	Weight (g) of Iron Powder Found:		
	In Bed	On Walls of Disengaging Section	On Filter ^a
Initial charge	446	0	0
Final calculated distribution ^b	385	76.6	12.4

^aSintered metal; median pore size, 40 μ .

^bFinal values were calculated using analyses of samples from the three locations. Difficulties in sampling were assumed to account for material-balance discrepancies.

solids can be withdrawn from any point within the column and discharged into an external transfer system. The conceptual design of this system requires that the circulating solids be returned to the reactor so that the sample tube may be swept out by fresh material for each sample. When the circulation of solids has been established, the flow can be stopped by the operation of valves, and the entire contents of the valved-off section of the circulation line can be drained into a sample container. This method is useful because a "normal" distribution of particle sizes can be established in the circulation line, and, by taking the entire contents of a line section, this size distribution will not be disturbed. Our data obtained from sampling T-60 alumina in the -48 +100 mesh size show the same size distribution in samples as in the alumina originally charged to the column.

When an added material of small particle size, such as iron powder or iron oxide, is used, the concentration of iron in the sample is related to the sampling location (vertically in the bed) and also the time after the start of fluidization. The increasing concentration of fine material at the top of the bed is a part of the elutriation process. The literature contains correlations of elutriation rate with particle size distribution, particle shape and surface characteristics, particle density, and gas flow rate; it also contains mixing rate correlations, based on the same properties. If we can obtain reliable and consistent data for particle size distribution by use of a carefully designed sampling system, these data combined with elutriation correlations may possibly yield a valid inventory analysis directly from fluidized-bed samples.

Postfluorination Sampling. - After the major portion of the uranium and plutonium have been volatilized from the fluidized bed, fission product fluorides, nonvolatile transuranium element compounds, and a small amount of residual uranium and plutonium remain. Such a mixture should not differ grossly from the alumina bed itself in particle size distribution, and a representative sample of the waste bed should be relatively easy to obtain. Since it is possible that fluorination will not have been complete and, consequently, that a large number of fine particles may remain, the techniques used for prefluorination sampling should be useful for the waste bed also. Use of the same sampler and procedures for both instances should be desirable in any event.

1.8 Corrosion Studies

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1.8.1 Intergranular Modifications of Nickel in Fluidized-Bed Volatility Process

Last year we reported results of studies made at Battelle Memorial Institute - Columbus Laboratories (under subcontract) to explain intergranular modifications of nickel exposed to fluidized-bed volatility process conditions.¹⁷ This work was completed with the issuance of a

summary report;¹⁸ conclusions were that intergranular penetrations could be produced in nickel 200 and nickel 201 specimens by their exposure to static beds of some types of alumina (the fluidized-bed medium). The intergranular penetrations were revealed by metallographic examination (etchant--equal volumes of concentrated nitric and acetic acids). Exposure of nickel to Norton Regular and Norton 38 alumina at 520°C produced severe penetrations, while Norton RR and Alcoa T-61 aluminas did not cause significant modifications. The intergranular modifications are thought to be the result of a sulfur contaminant in the alumina. The results correlate satisfactorily with chemical analyses, except that Norton 38, a relatively pure grade of alumina, effected modifications almost as severe as those from the impure Norton Regular alumina.

A spot test that is sensitive to sulfur compounds showed a positive reaction to the grain boundaries of nickel coupons having modifications. Results of electron-beam microprobe analyses showed sulfur, iron, and oxygen at the surface of nickel specimens with intergranular modifications, but sulfur could not be detected to a significant depth at the grain boundaries.

Bend tests indicated some damage to the material from the standpoint of strength. Tensile measurements made at room temperature and at 520°C showed that the ultimate tensile strength and the elongation of the nickel specimen were reduced appreciably by the intergranular modifications.

Intergranular modifications formed in nickel after exposure to Norton 38 cannot be explained, but no difficulties should be encountered under process conditions if either Norton RR or Alcoa T-61, or an equivalent, is used.

1.8.2 Choice of Constructional Material for FBVPP Leaching Equipment

We continued the development and design studies of equipment for leaching waste solids after their discharge from the primary reactor in the FBVPP. The primary purpose of the leaching equipment is to verify the sampling methods that will be used to determine uranium, plutonium, and fission product contents of the waste solids. Based on

laboratory studies, a 13 M HNO_3 --0.1 M HF has been assumed as the leachant. Because of the corrosivity of this solution, an experimental program was initiated at Battelle Memorial Institute - Columbus Laboratories (BMI) to supplement earlier work on corrosion testing. Results of the first screening studies were reported last year.¹⁷

Exposures of test coupons were made under refluxing conditions in an all-Teflon container using Teflon support rods. The boiling point of the solution was about 120°C. Most test specimens were about 1/2 by 2 in. and were cut from welded strips unless otherwise indicated. Except for specimen C-11, which was 1 x 2 in. and welded lengthwise, the welds were across the short dimension. Except in the early tests of Corronel 230, the specimens were completely immersed in the liquid.

Table 9 lists results of tests made during this period, plus significant earlier results for comparison. The initial study made last year showed that some alloys, particularly those having high nickel and chromium contents, possessed superior corrosion resistance in the boiling HNO_3 - HF solution. The 24-hr scouting tests during that period indicated that Corronel 230 and Hanford 20, and perhaps some of the other Hanford alloys, should be given longer-term tests; the very high resistance of 100% chromium indicated that some high-chromium alloys such as 50-50 and 60-40 wt % chromium-nickel (designated NA 55 and NA 64) should be investigated. In the 240-hr tests, the Corronel 230 continued to show up well, with the actual corrosion rates being reduced by a factor of 2 or more over the 24-hr tests (see Table 9); such decreases in corrosion rate for extended periods are to be expected.

The NA 55 and NA 64 alloys also showed good resistance in 24-hr tests; in fact, they were superior to all the materials tested except chromium. Although very little data has been published concerning the properties of these alloys, they are known to have poor forging and workability properties. BMI corroborated this by performing forging tests on cast button samples of these alloys that were obtained from the Blaw-Knox Company. At 1700°F, the sample ruptured on the second pass, while a smaller sample appeared to work better at 750°F. Larger samples of NA 55 were obtained from the Universal-Cyclops Corporation for testing.

Table 9. Corrosion Tests on Possible Alloys for Construction of Leaching System for Primary Reactor Solids

Test solutions were all at boiling point (~120°C); values were obtained by weight loss (unless otherwise noted) and are reported in mils/month.

Alloy								13 M HNO ₃ -0.1 M HNO ₃ -0.1 M HF						13 M HNO ₃ -0.1 M HF-0.1 M Al(NO ₃) ₃	
Cr	Ni	Co	Mn	Fe	W	Mo	Cu	24 hr		48 hr		240 hr		24 hr	
(%)								Welded	Unwelded	Welded	Unwelded	Welded		Welded	Unwelded
								Specimen Designation							
								Condenser							
<u>Corronel 230</u>															
36	58	-	1	5	-	-	-	C-9	3.8		5.8				
								Vapor							
								C-5, C-5, C-19	22.3		21.2		9.1 ^c (7.5) ^{a,c}		
								C-7, C-7, C-20	22.5		21.9		7.7 ^c (6.0) ^{a,c}		
								Interface							
								C-11, C-13, C-11, C-13	26.9	20.6	25.8	18.7			
								Liquid							
								C-1, C-1, C-17	25.9		26.0		12.8 ^c (7.5) ^{a,c}		
								C-2, C-18	17.9				10.8 ^c (8.3) ^{a,c}		
								C-8, C-14	20.9	17.0					
								C-3	27.1		28.2				
								C-4, C-10, C-15	17.4 (15) ^a					3.9 ^c	3.8 ^c
								C-6, C-16	21.0						4.0 ^c
<u>Vitalium (rolled)</u>															
24	2.8	62.2	0.7	0.7	-	5.5	-	D-327, D-326, D-327, D-326	34.1	32.3				6.4 ^c	5.9 ^c
<u>Chromium</u>															
100	-	-	-	-	-	-	-	Cr-1		3.9					
<u>50-50 Cr-Ni</u>															
50	50	-	-	-	-	-	-	NA 55	5.6 ^c						1.7 ^c
<u>60-40 Cr-Ni</u>															
60	40	-	-	-	-	-	-	NA 64	8.0 ^c						2.0 ^c
<u>Haynes 21 (rolled)</u>															
28	2.5	62	-	2	-	5.2	-	H-21C		26.9					9.4 ^c
								H-21D		28.4					10.7 ^c
<u>Hanford 20</u>															
25	50	-	0.6	16	-	6	1	HW-1, HA-1, HW-1	17.1	34.5				5.1 ^c	
								HW-2, HA-2, HW-2	17.0	28.6				5.0 ^c	
								HW-3, HA-3, HA-3	26.7	29.2					5.1 ^c
								HW-4, HA-4, HA-4	27.0	27.0					5.2 ^c
<u>Hanford 17</u>															
25	50	-	0.6	21.5	-	1.5	-	17W-1	23.6					4.8 ^c	
								17W-3	24.1					4.8 ^c	
<u>Hanford 21</u>															
25	50	-	0.6	18.5	-	1.5	3	21W-1	23.9					5.2 ^c	
								21W-3	23.9					5.0 ^c	
<u>Hanford 22</u>															
22	25	25	0.6	20	-	6	-	22W-1	40.4					8.2 ^c	
								22W-3	41.3					8.6 ^c	
<u>309 SOb</u>															
23	13	-	-	54	-	-	-	12-1, 12-S-4, 12-S-1	90.0 ^b					14.3 ^c	10.9 ^c
								12-2, 12-S-3, 12-S-2	80.0 ^b					17.4 ^c	11.1 ^c
								12-S-5						12.5 ^c	

^a By micrometer.^b Knife-line attack.^c Data obtained during this reporting period.

Since certain ions such as Al^{3+} are known to complex fluoride ion and reduce corrosion, 24-hr tests were made in boiling 13 M HNO_3 --0.1 M HF --0.1 M $\text{Al}(\text{NO}_3)_3$ solution on the most promising alloys; 309 SCb stainless steel was included as an example of a less expensive and much more available alloy, even though it had relatively poor corrosion resistance. The data (Table 9) show that the aluminum ion is effective in reducing corrosion rates to about one-fourth or one-fifth of the rate in uninhibited solution.

At this time, Corronel 230 and HAP0 20 are leading candidate materials for the leaching equipment. However, plans for future work include further ten-day corrosion tests of the 50-50 wt % chromium-nickel material, plus a more thorough evaluation of its mechanical and fabrication properties. Ten-day corrosion tests of HAP0 20, as well as a few more readily available alloys of similar composition, are also to be made.

2. STATUS OF THE FLUIDIZED-BED VOLATILITY PILOT PLANT

R. P. Milford

2.1 Flowsheets

C. C. Littlefield	W. A. Bush	S. Mann
E. L. Youngblood	F. W. Miles	R. G. Nicol
	W. H. Carr	

2.1.1 Chemical

During this period the fluorination portion of the chemical flowsheet was changed. Whereas in the previous procedure fluorine was used to volatilize both UF_6 and PuF_6 , the present method employs two steps: first, fluorination with BrF_3 is used to form UF_6 , and then fluorination with fluorine is used to form PuF_6 . According to the present flowsheets, the pilot-plant operation will consist of the following steps:

1. Removal of the Zircaloy cladding from the fuel element by reaction with anhydrous HCl at 400°C , followed by conversion of the volatilized ZrCl_4 to ZrO_2 with superheated steam in a separate fluidized-bed reactor at 350°C .

2. Oxidation of the remaining UO_2 - PuO_2 pellets in the primary reactor by contacting oxygen-nitrogen mixtures (or air) at 450°C to pulverize the ceramic pellets and to form U_3O_8 .
3. Fluorination of the uranium and plutonium oxides with BrF_5 to form volatile UF_6 and nonvolatile PuF_4 . The resulting bromine and traces of BrF_3 are converted to BrF_5 by reaction with fluorine. The UF_6 is partially decontaminated as it passes through a 400°C bed of NaF pellets. The BrF_5 and UF_6 are condensed in a cold trap.
4. Batch distillation of the mixture of BrF_5 , UF_6 , and volatile impurities (after its transfer from the cold trap) to yield high- and low-boiling fission product fluorides and various fractions of BrF_5 , UF_6 plus TcF_6 and NpF_6 , and mixtures of these. Further decontamination of the UF_6 is achieved by passing it through a bed of NaF at 400°C and through MgF_2 at 100°C ; the latter treatment removes technetium and neptunium hexafluorides.

The remainder of the chemical flowsheet, purification and recovery of plutonium, is still being studied at ANL and, to a lesser extent, at ORNL. The anticipated date for determination of a plutonium processing method is February 1967. At the end of the present period, several possibilities existed, of which the two leading prospects were: (1) a combination of cold trapping, sublimation, and thermal decomposition; and (2) sorption-desorption using a bed of LiF pellets at temperatures of about 300 and 500°C for the respective steps.

2.1.2 Engineering

The engineering flowsheet, as presently envisioned, is shown in simplified form in Fig. 21. The primary reactor and pyrohydrolyzer system remained essentially unchanged during this period, except that the primary and backup filters were combined into single housings for each vessel. The basic reactions of decladding, oxidation, and

ORNL DWG. 66-10255 R-1

Fig. 21. Flowsheet for Fluidized-Bed Volatility Pilot Plant
(as of November 30, 1966).

fluorination with BrF_5 and fluorine still take place in the primary reactor. The process gas leaving the reactor follows a different path for each step (see Fig. 21). In the further processing of the $\text{BrF}_5\text{-UF}_6$ stream, these two components plus some fission products are condensed or cold trapped and held in intermediate storage before distillation. Bromine pentafluoride will be recycled to the extent that distillation will permit; in a somewhat similar manner, fluorine will be recycled from the plutonium recovery step to the extent that dilution by nitrogen will permit. Most of the product recovery and purification equipment will be located in cell 2 of Building 3019, while the primary reactor and pyrohydrolyzer will be placed in cell 3.

The leaching system to be utilized as an analytical adjunct to the operation is not a true part of the process and is not shown in Fig. 21. The equipment is rather conventional and is intended to recover uranium and plutonium from waste solids, particularly from the primary reactor. It will be located entirely in cell 3, along with the primary reactor and the pyrohydrolyzer system, and will consist essentially of a combination of storage and head tanks for gravity circulation of leach solution [13 M HNO_3 , possibly buffered with $\text{Al}(\text{NO}_3)_3$], an upflow leacher, and an air lift to return overflow from the leacher to the head tank. After the waste solids have been discharged from either the primary reactor or the pyrohydrolyzer into a waste can attached to the appropriate reactor, the waste can will be moved and attached to the bottom of the leacher, where it will act as a temporary part of the leacher vessel.

2.2 Equipment Design

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At the start of this period, the equipment layout in cell 3 for the all-fluorine flowsheet had been reasonably well defined, and piping drawings were about 75% complete. The adoption of the interhalogen flowsheet entailed some major changes in layout and virtually a new

approach in piping. The so-called reactor cubicle (the shielded alpha compartment within cell 3 to house the reactor and pyrohydrolyzer) was not altered, partly because of the advanced stage of fabrication. The location of the reactor and the conceptual design for the equipment manipulator within the cubicle were virtually unchanged, but almost all other features of the layout were revised considerably. By the end of this period, new layout drawings for cell 3 had been completed; these included the leaching system that was originally located in cell 1.

Drastic revision was made of several individual design features, principally: (1) the aforementioned combining of primary and backup filters into the same housing for both reactor and hydrolyzer, and (2) the use of thin-walled metal cans instead of plastic bags to contain equipment while it is being transferred into and out of the cells. An example is the reactor-solids waste cans.

The location of primary and backup filters in a common housing was based on more complete test data showing higher permeability characteristics, with a corresponding reduction in filter area being required. This change greatly simplified the design of the filter removal parts in the cell roof. The tests, which were conducted by the Engineering Development Department at ORGDP, also verified that the Huyck Corporation metal fiber filters (compared with sintered metal-powder filters) show general superiority in mechanical properties (strength), uniform porosity, capacity drop during operation, etc. The canning technique, which is being used for transferring equipment to or from the cells, is simpler with respect to equipment and operations than the bagging method and greatly reduces contamination hazards.

The design of the ventilation system for cell 3 is about 80% complete. No decision was reached on the need for in-cell scrubbing (or alternative treatment) for the ventilation air. The design of the shielded glove box for charging fuel to the reactor is virtually complete, and work is under way on the design of the equipment for loading fuel carriers at the storage canal. Many details of the design of the equipment manipulators to be located in cell 3 cannot be completed until the layout is completed. The layouts for many smaller vessels and

various sampling stations are still in an early stage of development.

The instrumentation and the design of the electrical features are keeping pace with the rest of the program.

2.3 Construction

G. E. Pierce

J. T. Huffstetler

B. B. Klima

2.3.1 Equipment Fabrication

Fabrication is complete for the process off-gas scrubber system and the BrF_5 - UF_6 cold trap; it is almost complete for a number of major items, including the primary reactor and filter assembly, the pyrohydrolyzer, and the fluorine compressor. Most of the gamma shielding sections for cell 3, the nitrogen blowback surge tank, two chemical (NaF pellet) traps, and the reactor-outlet gas cooler have been fabricated; the latter item of equipment is ready for heat-transfer measurements.

2.3.2 Equipment Installation

All penetrations from cell 3 to other areas have been drilled. This proved to be much more costly and time-consuming than predicted because of insufficient ruggedness of drilling equipment. No new penetrations have been drilled for cell 2, which is still in the cleanout stage.

The process off-gas scrubber has been installed and shielded, but the caustic pump has not yet been received. Curbing and floor sheathing have been completed in cell 3. Gamma shielding and alpha sealing for the reactor cubicle are about 80% complete at the first level, which less progress has been made at the higher levels. Numerous supports for vessels and shielding are already complete, and lead-brick shielding for the UF_6 cold trap is partly installed.

2.3.3 Costs and Scheduling

The project plan has been revised three times in the past two months. At present, the expected completion date for both cells 2 and 3 is

is August 26, 1968. The current limiting activity is the purchase of orifices.

2.4 Criticality, Hazards, and Plutonium Handling

E. L. Youngblood

F. W. Miles

As the design of the pilot plant progresses, we are continually studying various hazards and potential situations involving criticality. Separate reports will be issued on criticality and on operating and chemical hazards. One significant area from the standpoint of criticality is the process off-gas scrubber. Its caustic surge tank must be poisoned; at present, the use of a soluble rather than fixed poison is planned. Preliminary tests have shown that concentrations of 22 to 23 g of B^{3+} per liter can be obtained, compared with a calculated requirement of 20 g/liter. However, since precipitation of the poison is possible, the choice of the type of poison is not final. In other areas (e.g., the primary reactor and the cold traps), measures will be taken to protect against the admittance of moderating materials such as liquid HF or fluid from a coolant system. Also, the amount of fissionable material in the system will be carefully regulated.

Chemical hazards from materials such as BrF_5 and fluorine cannot be fully evaluated until the engineering flowsheet is further advanced. However, protective measures, where evident, have already been designated; one example is the enclosure planned for the instrument transmitter rack. At present, no specific rules have been defined for plutonium handling, except that neither plutonium nor uranium is to be deliberately discharged to the various scrubbing systems.

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