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ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

*Part 2. Bench-scale Investigation of a
Process for Aluminum-Uranium Alloy
and Stainless Steel-Cermet Fuels*

by

D. Ramaswami, N. M. Levitz, and A. A. Jonke

Chemical Engineering Division

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- Part 3: Fluid-bed Fluorination of Uranium Dioxide Fuel Pellets, by L. J. Anastasia, J. D. Gabor, and W. J. Mecham (ANL-6898)
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ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 2. Bench-scale Investigation of a Process for Aluminum-Uranium Alloy and Stainless Steel-Cermet Fuels

by

D. Ramaswami, N. M. Levitz, and A. A. Jonke

ABSTRACT

As part of a continuing program on the development of fluid-bed fluoride volatility processes, methods were developed for reprocessing highly-enriched uranium-aluminum alloy and uranium dioxide-stainless steel cermet fuels. These methods involve two basic gas-solid reaction steps: a separation step, in which the cladding, the bulk constituent of the fuel, is separated from the uranium, a minor (<10 w/o) constituent of the fuel; and a fluorination step, in which the uranium is recovered through the production of the volatile hexafluoride. The reactions are conducted in a fluid bed of high-fired alumina, which serves as a heat-transfer medium. Processing of these two types of fuels differs mainly in the initial separation step: Hydrogen chloride is used to remove the aluminum as the volatile chloride; the hydrogen fluoride-oxygen mixture is employed to destroy the stainless-steel matrix by producing an oxide mixture which remains with the alumina.

Process studies were conducted in a $1\frac{1}{2}$ -in.-diam nickel fluid-bed reactor with miniature nonirradiated fuel subassemblies. More than 99% of the uranium in the fuel charge was recovered over a range of processing conditions.

The current work, along with the previous work, summarized in a companion report (ANL-6829), has demonstrated the applicability of fluid-bed fluoride volatility methods to the processing of highly-enriched fuels of current interest. Considerable economic advantage of this process over the current aqueous reprocessing schemes appears possible because overall fewer and simpler operations are needed and smaller volumes of high-level radioactive wastes are produced.

SUMMARY

Development work was completed on the two basic chemical-reaction steps of a fluid-bed fluoride volatility (FBV) process for the recovery of uranium from highly-enriched uranium-aluminum alloy (U-Al) and uranium

dioxide-stainless steel cermet ($\text{UO}_2\text{-SS}$) fuels. The studies concerned investigation of (1) the separation step in which uranium, a minor constituent, is freed from the bulk constituents of the fuel; and (2) the fluorination step in which the uranium is subsequently converted to the volatile hexafluoride. The reactions are conducted in an inert fluidized bed, comprised of high-fired alumina, that serves as a heat-transfer medium.

For the separation of uranium from the bulk constituents of the fuel, the aluminum of the U-Al fuels, by reaction with HCL, is volatilized as its chlorides, while the uranium is converted to its nonvolatile chlorides and is retained in the system. The stainless steel of the $\text{UO}_2\text{-SS}$ fuels, by catalysis in the presence of HF, is destructively oxidized to flakes which mix with the alumina along with the uranium compounds.

Subsequently, for the recovery of uranium, the systems are treated with fluorine, the volatile product, UF_6 , is recovered in cold traps maintained at dry-ice temperatures. During fluorination, the oxide scales from the cermet fuels are converted to particulate fluorides. Particulate material entrained from the fluid bed by the exit gas stream are retained in the reactor system by a packed bed of high-fired alumina.

Process development work, using miniature nonirradiated fuel sub-assemblies, was conducted in a $1\frac{1}{2}$ -in.-diam fluid-bed reactor system. More than 99% of the uranium in the fuel charge was consistently recovered under a variety of processing conditions. The uranium recoveries were unaffected by the presence of cladding and fission-product elements. The small amount of uranium lost was that in the gas stream exiting the packed-bed filter during the hydrochlorination of the U-Al fuels and that in the alumina beds discarded at the end of the fluorination. These two losses averaged 0.1 and 0.4% of the uranium in the initial charge, respectively. Concentrations of 0.01 w/o uranium in the beds after fluorination corresponded to this level of loss.

To establish the magnitude of the effects of all processing conditions and the amount of uranium retained by alumina at the end of the fluorination step, the following semiempirical relationship was derived, which correlates the experimental data with an error of $\pm 40\%$. The weight percent of uranium, W , in the alumina bed was represented by

$$W = 0.0000573 \frac{t p_{\text{UF}_6}^{1.78} \exp(123.8/T)}{r^{0.56} p_{\text{F}_2}^{0.7}},$$

where t is the time during which 90% of the uranium in the fuel charge is recovered; p_{UF_6} is the average partial pressure of UF_6 in the bed during time t ; T is the temperature of the bed during the final stage of fluorination; r is the rate of uranium recovery based on total fluorination time and p_{F_2} is the maximum partial pressure of fluorine the alumina was exposed to.

This relationship is applicable for concentrations of residual uranium in the range of 0.002 to 0.06 w/o and in the following ranges for the operating conditions:

- t: from 0.2 to 4.0 hr,
- PUF_6 : from 1.1 to 22 mm Hg,
- T: from 623 to 773°K,
- r: from 0.0016 to 0.028 kg of uranium per hr kg of alumina,
- pF_2 : from 0.6 to 1.2 atm.

The derivation of this relationship also included data from the previous studies on the development of a process for uranium-zirconium alloy (U-Zr) fuels (ANL-6829).

Hydrogen chloride utilization was higher when alumina of a wide size distribution (40 to 100 mesh) was used as fluid-bed material than when alumina of a narrow size distribution (80 to 100 mesh) was used. Under the best operating conditions, ~2.5 stoichiometric amounts of HCl were needed to convert the base metal to its volatile chloride. Both fused and sintered grades of high-fired alumina were satisfactory as bed materials, in that they did not cake and remained fluidizable throughout the reaction cycle.

During the process, distribution of the minor constituents of the fuel and of simulated inactive fission products added with the fuel conformed to that estimated from the volatilities of their higher valent chlorides and fluorides. The behavior of the fission products indicates that partial decontamination is achieved during each step, and, based on present technology for the final decontamination of the UF_6 , a high-purity UF_6 product can be produced by the FBV process.

Recommended operating conditions for processing U-Al and UO_2 -SS fuels are:

Fluid-bed material: High-fired alumina (fused or sintered type), nominal 40-mesh size, sufficient to cover the fuel elements.

Separation step

U-Al fuels: Temperature of fluid bed: 200-300°C; Concentration of HCl: 5 to 75 v/o as desired to maintain high reaction rates.

UO_2 -SS fuels: Temperature of fluid bed: 550°C; Composition of the feed gas: 40 v/o HF, 40 to 60 v/o oxygen, and 20 to 0 v/o nitrogen.

Fluorination step: Gradual increase in temperature from 250 to 500°C while the reactor bed is being fluidized with 5 to 10 v/o fluorine in nitrogen; then gradual increase in fluorine concentration to 90 v/o. The alumina may be fluidized or maintained static during the final cleanup period.

Packed beds, 10 to 12 in. deep, of alumina, -14 +20 mesh size, maintained at 180 to 200°C while the U-Al fuels are being hydrochlorinated and at 100°C while the UO₂-SS fuels are being destructively oxidized, may be used as filters. Following the hydrochlorination of the U-Al fuel, a hydrofluorination step of 1-hr duration at about 275°C, with HF concentrations of 20 to 50 v/o (found to have no effect on uranium recovery from alumina beds) may be employed to remove the chloride associated with the alumina beds before they are exposed to fluorine. The durations of the separation and fluorination steps may be 4 to 8 hr, depending on the quantity of fuel charge.

Separation and fluorination conditions for recovering uranium from the most commonly used highly-enriched nuclear fuels by FBV processes have now been established. The scheme for processing highly-enriched U-Zr fuels has been described in ANL-6829. Process demonstration and supporting work have been presented in ANL-6973, ANL-6992, and ANL-6994. An oxidation-fluorination scheme for reprocessing enriched uranium dioxide or uranium carbide dispersed in a graphite matrix has been developed at Brookhaven National Laboratory (BNL-867, p. 102).

The FBV process appears to offer considerable economic advantage over the current aqueous reprocessing schemes because overall fewer and simpler operations are needed, and smaller volumes of high-level radioactive wastes, mostly in solid form, are produced. Further, fuels decayed for a short time, or fuels with very high burnup, can be processed by the FBV process; these fuels, because of their high radioactivity, damage the organic solvents used in the aqueous processes.

I. INTRODUCTION

Highly-enriched uranium fuels are used in a variety of nuclear reactors where large energy sources of small mass are needed. For example, U-Al fuels in research, test, and training reactors;¹ U-Zr fuels in submarine reactors;² UO₂-SS fuels in stationary and medium power plants.³ These nuclear fuels are mainly in the form of multiplate subassemblies.^{3,4}

Fuels discharged from nuclear reactors, as well as those scrapped in fuel-fabrication facilities, are being reprocessed by aqueous methods, which involve solvent-extraction techniques.⁵ The aqueous methods produce large volumes of radioactive liquid wastes, which cause storage and

handling problems. Minimization, if not elimination, of these aqueous, radioactive wastes is desirable. Consequently, a program to evaluate the potential of fuel-reprocessing methods using fluid-bed volatility techniques was undertaken to overcome the problems inherent in the aqueous processes.

The FBV reprocessing consists, basically, of (1) a separation step to free the uranium from the fuel matrix, followed by (2) a fluorination step to recover the uranium as the hexafluoride, and then (3) a decontamination step, distillation^{6,7} or adsorption-desorption using NaF pellets,⁸ to separate the UF_6 from fission products and other minor contaminants. The refined UF_6 is converted to uranium metal or oxide for the manufacture of new fuel.²

The technology of the separation and fluorination steps has been developed at ANL. The bench-scale development of these steps for the recovery of uranium from U-Zr fuels has been outlined in a previous report (ANL-6829), and similar work with U-Al and UO_2 -SS fuels is summarized in the current report.

The separation and fluorination reactions are highly exothermic, and these are controlled by using fluid-bed systems with favorable heat-transfer properties. High-fired alumina, demonstrated to be inert and suitable as a bed material while the U-Zr fuels are being processed, is fluidized by the reagent and diluent gases.

The chemical reactions involved in the separation step are carried out while the fuel is immersed in a fluid bed of alumina. The U-Al fuels are reacted with HCl; the aluminum is converted to its volatile chlorides, while the uranium is converted to nonvolatile chlorides. The off-gas, consisting of Al_2Cl_6 and $AlCl_3$, hydrogen, excess HCl, and diluent nitrogen, is passed through a heated packed bed of alumina, which serves as a high-temperature filter to retain entrained particulate uranium chlorides; the gas stream exiting the filter is treated and exhausted. The UO_2 -SS fuels are exposed to gas mixtures of HF and oxygen; the stainless steel is destructively oxidized to scaly products, and the uranium dioxide is converted to higher-valent "oxides and fluorides." The scaly products, along with the uranium compounds, remain in the reactor system.

After the separation step, the uranium compounds, along with the residual compounds of the cladding material in the alumina beds, are exposed to fluorine. The resultant volatile fluorides, with UF_6 as the major component, are recovered.

The bed material is discarded after one or more process cycles because of (a) the buildup of the heat and radioactivity from accumulated fission products, and (b) the accumulation of nonvolatile, fluoride, matrix and fission-product materials. Hence, uranium retained in these waste beds is a loss. The uranium carried away by the gas stream exiting the filter during the hydrochlorination of the U-Al fuels is also a loss.

The main objective of the current study was to establish process conditions that would result in minimal uranium losses. The other objectives were (a) to determine the distribution of the fission products and other constituents of these fuels, (b) to establish the suitability of packed beds of alumina as high-temperature filters during the hydrochlorination of the U-Al fuels, (c) to study the behavior of alumina during the two steps, and (d) to determine the corrosion rates of Nickel-200 in the process environments.

II. LITERATURE REVIEW

A. Process Chemistry

Most of the basic data on the physical and chemical properties of the systems encountered in the current FBV process development work are available in the literature. Consequently, only the information needed for discussion in this report is presented in the following; for additional information, see the references cited.

1. The Separation Step

a. Hydrochlorination of Uranium-Aluminum Alloy Fuels. As an initial step of the FBV process, the U-Al fuels are reacted with HCl while they are submerged in an inert (alumina) fluid bed maintained at temperatures above 180°C (the sublimation point of AlCl_3 at 1 atm). The aluminum is converted to the volatile trichloride by the following reaction:

The AlCl_3 in the vapor phase associates into a dimer, Al_2Cl_6 ; the extent of association depends on the temperature and total pressure, and at 180°C and 1 atm, more than 99.9 w/o of the chloride in the vapor phase represents the dimer. The physical and thermodynamic properties of the aluminum chlorides are summarized by Blander et al.⁹ Properties of HCl, hydrogen, HF, fluorine, nitrogen, and oxygen used in the current work are available in the Matheson Gas Data Book.¹⁰

The following reaction of uranium and HCl produces UCl_3 (mainly) and UCl_4 :

The uranium chlorides become particulates since their melting points (842 and 590°C, respectively, for UCl_3 and UCl_4) are considerably higher than the temperatures at which the fluid bed is operated. The vapor pressures of these chlorides at fluid-bed temperatures are very low (e.g., 5×10^{-10} and 3.7×10^{-4} mm Hg for UCl_3 and UCl_4 at 350°C, respectively), and therefore the off-gas stream should contain only trace quantities of uranium as vapor. The thermochemical data, along with physical properties of the uranium-chlorine compounds, are reviewed by Katz and Rabinowitch,¹¹ and the experimental data on the vaporization of chlorides of pertinent elements are compiled by Feber.¹²

The uranium chlorides in the system may be reacted with HF as follows to displace the chloride prior to exposure of the system to fluorine:

b. Destructive Oxidation of Uranium Dioxide-Stainless Steel Cermet Fuels. The UO_2 -SS fuels are exposed to HF-oxygen mixtures, while the fuels are submerged in fluid beds of alumina maintained at about 550°C . Iron, the major constituent of the stainless steel, is oxidized by the following reactions:

Due to these reactions, the stainless-steel cladding is destroyed and the UO_2 is exposed to the gas mixture causing:

2. The Fluorination Step

After the separation step, the system is exposed to fluorine, in the range of 250 to 550°C , to recover the uranium as its volatile hexafluoride (sublimation point for UF_6 : 56.5°C at 1 atm)¹³ in accordance with the following reactions:

The UF_6 may react with UF_4 to intermediate fluorides; these, in turn, may be fluorinated, the rate being dependent on the partial pressure of fluorine.¹⁴ Simultaneously with the above reactions, the following reactions proceed when the products of the destructive oxidation of stainless steel are present:

The chromium compounds in the oxidation products become fluorides or oxyfluorides, depending upon the temperature and concentration of fluorine.

B. Earlier Process Development Studies

Related process studies have been reported on four leading types of highly-enriched fuels.

1. Uranium-Aluminum Alloy Clad with Aluminum

The first experiment with U-Al fuels utilizing the current FBV process concepts was made in 1962 at ANL. The process development since then is outlined in this report.

After the development work with U-Al fuel was initiated at ANL, studies that complemented the work at Argonne were made independently in the laboratories at Brookhaven and Oak Ridge in the U. S., and at Fontenay-aux-Roses and Grenoble in France. At Brookhaven, this reprocessing method was explored by means of a $1\frac{1}{2}$ -in.-diam fluid-bed reactor.¹⁵ Hydrochlorination rates increased from 14 to 22 mg/(cm²)(min) when the temperature was raised from 250 to 400°C, with 60-mesh Alundum* fluidized by 100 v/o HCl at a gas velocity of 0.7 ft/sec. Fluorination of the bed after hydrochlorination reduced the concentration of uranium in the bed from ~5000 to 50 ppm. At Oak Ridge, computer calculations were made by means of "GHTR heat transfer code on IBM 7090."¹⁶ The results from these calculations indicated that "it will be possible to hydrochlorinate MTR fuel elements at rather low rates without exceeding the melting temperature of the fuel, 650°C." This conclusion is in accordance with the experimental data in the current bench-scale development work. In France, the results of development studies¹⁷ confirmed the results obtained at Argonne on uranium recoveries and process operating conditions; an example of the concurrent results is the reduction in the quantity of uranium contained in the gas stream exiting the packed-bed filter during hydrochlorination by lowering the reactor system temperatures, with the consequent achievement of higher uranium recoveries.

2. Uranium Zircaloy Alloy Clad with Zircaloy

Development work on the FBV process for U-Zr fuels was conducted in the laboratories at Brookhaven, at Fontenay-aux-Roses and Grenoble (in France), and at Argonne. A comprehensive survey of the work at ANL with nonirradiated fuel, up to 0.72 kg, in a bench-scale fluid-bed reactor, was presented in an earlier report.¹⁸ The FBV process conditions recommended by this bench-scale investigation were, subsequently, confirmed at ANL by the pilot-scale investigations¹⁹ made with 30-kg charges

*Fused alumina grain manufactured by Norton Co., Worcester, Mass.

of nonirradiated fuel subassemblies. Bench-scale studies with irradiated, highly-enriched, uranium-alloy fuels are also in progress at ANL and will be presented in a forthcoming report ²⁰

Processing of these fuels is similar to that described earlier for U-Al fuels except that, during the hydrochlorination, the temperatures of the fluid-bed reactor and the packed-bed filter are maintained above 331°C, the sublimation point of $ZrCl_4$ at 1 atm. More than 99% of the uranium in the fuel charge was consistently recovered under a wide variety of process operating conditions.

3 Uranium Dioxide Dispersed in Stainless Steel

During the development of the FBV process for stainless-steel clad, low enriched UO_2 fuels, several methods of decladding were investigated, but only limited success was achieved. Examples of these methods are: high-temperature chlorination of stainless steel at BNL²¹ and ANL,²² aqueous hydrochloric acid corrosion in beds of alumina fluidized by air at ANL,²³ and catastrophic oxidation of stainless steel promoted by solid fluorides at BNL.²⁴

Tests at Oak Ridge²⁵ in 1964 established that the presence of HF promoted the destructive oxidation of stainless steel at temperatures of 600 to 700°C, and penetration rates to 67.5 mils/hr were attained with 40 v/o HF in oxygen at 650°C. These studies were directed toward the use of fused-salt systems in the reprocessing of power reactor fuel; as such fluid beds were not used.

As a consequence of the results at Oak Ridge, the initial destructive oxidation tests in the presence of fluid beds of sintered alumina were made at Argonne²⁶ in 1964. The penetration rates for Type 304 stainless steel were ~30 mils/hr at 550°C with 40 v/o HF in oxygen. The latter tests at Argonne were directed toward processing of the highly enriched stainless steel cermet fuels, and further development of this method of decladding stainless steel-clad low enriched UO_2 fuels is continuing at BNL.

4 Uranium Dioxide and Carbide Dispersed in Graphite

The FBV process for recovering uranium from uranium dioxide and carbide dispersed in graphite was developed at Brookhaven National Laboratory ^{21,24,27}. The process for these fuels consists of two steps similar to the separation and fluorination steps for the other highly-enriched fuels. But two separate fluid bed reactors (4-in diam), connected via pneumatic solid-transfer line, were used for the two steps in this work with nonirradiated fuels. In the first reactor, the matrix was transformed to CO_2 gas,

and the uranium to U_3O_8 particulate, by reaction with oxygen at a gas velocity of 1 ft/sec and a bed temperature of 750°C. In the second reactor, the transferred bed containing the U_3O_8 was exposed to 25 v/o fluorine in argon, at a gas velocity of 0.5 ft/sec and a bed temperature of 450°C. The volatile UF_6 thus produced was recovered, and recoveries of uranium were >99% of that in the fuel charge.

III. EQUIPMENT AND PROCEDURE

A. Equipment

The equipment included a $1\frac{1}{2}$ -in.-diam reactor assembly, a gas feed system, and auxiliaries for handling the reaction products and off-gases. The reactor assembly consisted of a fluid-bed reactor and a packed-bed filter; both vessels were made of Nickel-200. The reactor was made up of three separate sections joined by flanges: (1) the bottom section, consisting of an inverted 60° cone with a single $1\frac{1}{4}$ -in.-IPS connection at the apex for feeding gases and draining beds; (2) the fluid-bed section, a 14-in. length of 1.5-in.-IPS pipe; and (3) the disengaging section, a 14-in. length of 3.0-in.-IPS pipe, with its lower end necked down to mate with the fluid-bed section. The packed-bed filter, a 14-in.-long section of 1.5-in.-IPS pipe containing granular alumina as the filter media, was connected to the reactor by a horizontal 1-in.-IPS pipe; the ends of the connecting pipe have tee connections, usable as charging ports. The reactor, the filter, and the connecting pipe were provided with the necessary heaters, cooling coils, and controls for operating at temperatures to 650°C .

Auxiliary equipment used during the separation step included apparatus to provide HCl with desired moisture content, to condense the aluminum chlorides, to dispose of excess HCl, and to supply and dispose of HF. Auxiliary equipment used for the fluorination step included UF_6 cold traps in a dry-ice trichloroethylene bath (-78.5°C) and a fluorine disposal tower. The gas supplies for the commercial-grade HCl, HF, oxygen, fluorine, and nitrogen (for dilution, purges, and fluidizing purposes) were manifolded. Thermal-conductivity cells, used to follow the progress of the reactions by monitoring for key components in the off-gases from the reactor assembly, were provided with nickel filaments.

The equipment and operating procedure were described in detail previously (ANL-6829, pp. 18-24). The reactor assembly and the auxiliary equipment are shown in Fig. 1 as installed for operations in a vacuum-frame hood.

B. Experimental Procedure

The experimental procedure included prefluorination, separation, and fluorination steps. After each step, the reactor system was purged with nitrogen. The appropriate items of auxiliary equipment were then installed, and the operating sequence continued.

Samples of the bed and various streams were taken to determine the distribution of uranium and other pertinent elements at various stages of the process.

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Fig. 1. Bench-scale Fluid-bed Reactor System

IV. THE SEPARATION STEP

A. Hydrochlorination for Uranium-Aluminum Alloy Fuels

The U-Al fuel-element subassemblies, immersed in a fluid bed of alumina, are reacted with HCl at bed temperatures of 180 to 400°C. The resultant volatile aluminum chlorides are carried out of the fluid bed by the exiting gas stream, and the nonvolatile uranium chlorides (UCl_3 and UCl_4) are retained mostly in the fluid-bed reactor. A minor amount of the uranium chlorides is entrained by the gas stream leaving the fluid bed. Any uranium that is not filtered from this chloride gas stream is a loss since all the chlorides in this stream are pyrohydrolyzed to solid oxide waste, and the uranium in this waste is not recoverable. Establishing the process conditions that result in minimal amounts of this uranium loss was an objective of the current investigation, and packed beds of alumina, to filter the uranium particulates, were tested. The ranges of operating conditions investigated in this study are shown in Table I, and the details of specific runs are given in the appendix in Tables XII and XIII.

TABLE I. Ranges of Hydrochlorination Conditions Investigated for Uranium-Aluminum Alloy Fuels

<u>Fuel Charges</u>	
Weight:	160 to 240 g of alloy (1 to 3 charges per run), 13.7 g of simulated fission products;
Concentration of uranium:	3 to 5 w/o;
Shapes:	chips, 1/8- to 1/4-in. size; and miniature fuel-element subassemblies.
<u>Alumina Charges</u>	
Fluid bed:	High-fired aluminas (sintered and fused types), 320 g, 40- to 120-mesh sizes;
Packed-bed filter:	Sintered and fused aluminas, -14 +20 mesh, 6 to 12 in. deep with downward gas flow.
<u>Temperature</u>	
Fluid bed:	180 to 400°C;
Fluid-bed reactor wall:	180 to 260°C;
Packed-bed filter:	180 to 230°C.
<u>Reactant Conditions</u>	
HCl concentration:	0 to 75 v/o;
Quantity of HCl:	2.3 to 3.6 stoichiometric amounts needed to convert aluminum to its trichloride;
Moisture content of HCl:	0 to 1100 ppm;
Concentrations of hydrogen in HCl:	0 and 20 v/o.

1. Uranium Loss through the Packed-bed Filter

Indications were that the overall problem of retaining uranium compounds in the reactor assembly may not be one of filtration alone, but a combination of filtration and condensation of volatile species, during the U-Al runs, just as in the case of U-Zr fuel hydrochlorinations (ANL-6829, page 27). Since the condensation of the "volatile uranium species" was effectively achieved by maintaining the packed-bed filter at the lowest practicable temperature (330 to 350°C) while the U-Zr fuels were being processed, the filter was kept at the lowest practicable temperature (~180 to 200°C) while the U-Al fuels were being hydrochlorinated.

The quantity of uranium in the gas stream exiting the packed-bed filter was determined as a function of bed depth. The uranium loss decreased to <0.2% of that in the fuel charge as the depth was increased to ~10 in. (see Fig. 2 and Table II); the loss remained at this value al-

Fig. 2. Effect of Packed-bed Filter Depth on Filtration Efficiency

Bed Material: Granular Alumina, -14 +20 Mesh
Gas Velocity: 0.5 to 0.7 ft/sec
Temperature: 180 to 200°C

though the depth was further increased to 12 in. Also, the filtration efficiency (defined as the percent of the uranium load on the filter retained by it) increased steeply to 99.4% with increase in the packed-bed depth to about 8 in., and then gradually levelled off to 99.6%, indicating that bed depths of 10 in. may be sufficient.

The possible reduction of volatile uranium chlorides, if any, present in the off-gas from the filter by feeding hydrogen along with HCl was explored in one of the runs. The presence of hydrogen in the feed HCl did not reduce the uranium loss to the aluminum chloride condenser, and the concentrations of uranium collected in the condenser were 5.0×10^{-5} and 3.4×10^{-5} g of uranium per gram of aluminum, respectively, with and

without the hydrogen (20 v/o) in the HCl.

2. Overall Utilization Efficiency of Hydrogen Chloride

The effects of the particle size of the fluid-bed alumina, the plate spacing of the fuel-element subassemblies, and the moisture content of feed HCl on overall utilization of HCl were investigated in a series of runs with both U-Zr and U-Al fuels to optimize the hydrochlorination conditions.

TABLE II. Filtration of Uranium Chloride Particles
by Packed-bed Filters

Bed material:	Granular alumina, -14 +20 mesh; ^a approximately 53.3 g/in. of bed (random-loose to random-dense packing) depth.
Diameter of filter:	1.5 in.
Temperature:	180 to 200°C
Velocity of gas:	0.5 to 0.7 ft/sec
Direction of gas flow:	Down
History of uranium particulate:	Produced in a fluid bed at 190 to 400°C by hydrochlorination of U-Al fuel (for further details, see Tables XII and XIII).

Run No.	Uranium Reacted, g	Uranium Load on the Filter, g	Filter Bed Depth, in.	Filter		
				Uranium Passed Through		Filtration Efficiency, %
				g	Percent of Uranium Reacted	
A-1	2.2	0.64	0	0.640	29.1	0
			3.2	0.189	8.6	70.5
			5.4	0.063	2.86	90.2
			6.0	0.046	2.09	92.8
Al-2	6.9	1.17 ^b	6.0	0.084	1.22	92.8
Al-3	8.9	1.51 ^b	8.0	0.0089	0.1	99.4
Al-4	6.9	1.17 ^b	12.0	0.0099	0.14	99.6

^aFor Al-1, 120 g of -40 +60 mesh alumina was sandwiched between 170 g, at top, and 30 g, at bottom, of -14 +20 mesh alumina.

^bTo exclude the effect of fuel shape on the uranium load, the load was assumed to be the average amount of uranium, 17% of that in the charge, recovered by fluorination of the filter separately from the fluid bed after the hydrochlorination of U-Zr fuel subassemblies during two runs.

The utilization of HCl increased with decrease in the ratio of plate spacing to average particle diameter and with increase in the particle-size distribution of alumina. While the U-Zr fuel-element sub-

Fig. 3. Effect of Ratio of Fuel-plate Spacing to Alumina Particle Diameter on Hydrogen Chloride Required

rather than uniform, particle sizes. Similar effects were observed while the U-Al fuels were being hydrochlorinated.

assemblies with same plate spacing were being hydrochlorinated, the ratio was decreased from 12.0 in Run Zr-39 to 4.7 in Run Zr-41, and the quantity of HCl needed to complete the reaction was considerably lower in the latter run than in the former run, 2.9 as compared to 9.0 stoichiometric amounts (see Fig. 3 and Table III). To complete the hydrochlorination of the same-sized fuel elements, 9.0 stoichiometric amounts were required when -80 +100 mesh alumina was used (Run Zr-39), whereas only 4.6 stoichiometric amounts were needed when a mixture of -80 +100 and -40 +60 mesh alumina was used; this improvement in the HCl utilization efficiency might have been due to the better quality of fluidization of alumina with mixed,

TABLE III. Effect of Ratio of Fuel-plate Spacing to Alumina Particle Diameter on Hydrogen Chloride Required

Run No.	Granular Alumina Mesh Size	Type	Plate Spacing, in.	Ratio of Plate Spacing to Av Particle Diam	Quantity of HCl, amounts stoichiometric	Moisture Content of HCl, ppm
Zr-39	-80 +100	38 ^d	5/64	12.0	9.0	1100
Zr-38	-84 +100	38 ^a	5/64	12.0	8.7	35
Zr-37	-40 +60	RR ^a	1/8	9.5	5.0	-
Zr-40	-40 +60 50 w/o -80 +100 50 w/o	38 ^a	5/64	8.2	4.6	1100
Al-2	-80 +100	38 ^a	1/20	7.8	3.6	35
Al-3	-40 +120	T-61 ^b	1/20	5.0	3.0	1100
Zr-41	-30 +60	T-61 ^b	5/64	4.7	2.9	1100
Zr-42	-40 +60	T-61 ^b	1/16	4.75	2.9	1100
Al-4	-40 +120	T-61 ^b	1/20	4.7	2.5	1100

^a Alundum, manufactured by Norton Company.

^b Tabular alumina, manufactured by Aluminum Company of America.

Moisture in HCl, in amounts to 1100 ppm (similar to that in the off-gas recycle system; ANL-6829, p. 48), did not affect the overall utilization efficiency (see Table III); about 3.0 stoichiometric amounts of HCl were needed to hydrochlorinate either type of fuel completely.

3. Displacement of Residual Chloride by Hydrofluorination

At the end of hydrochlorination, the uranium chlorides in the reactor assembly, before their exposure to elemental fluorine, may be converted to the tetrafluoride by reaction with HF; otherwise, fluorine produces volatile interhalogen compounds, along with UF_6 , which condense in the cold traps, and the hydrolysis of this mixture for determining uranium material balance in experimental facilities was hazardous (ANL-6596 p. 151).

The effect of fluid-bed temperature during hydrofluorination on the residual chloride content of the bed was determined in one of the runs by analysis of the bed samples taken at the end of a hydrofluorination period at each of three temperatures. The results indicate that the chloride content was reduced from 0.77 to 0.15 w/o at 200°C, then decreased to 0.03 w/o at 275°C, and further decreased to 0.006 w/o at 350°C. The two concentrations at the higher temperatures are similar to those resulting from the direct exposure of the beds to fluorine. The HF concentration in the feed stream was 50 v/o in this run, and the final chloride contents of the bed were similar in other runs with different HF concentrations. The incorporation of hydrofluorination into the reaction cycle did not affect the overall uranium recovery.

B. Destructive Oxidation for Stainless Steel-cermet Fuels

The FBV process for UO_2 -SS fuels involves destructive oxidation of the stainless steel in fluid beds of alumina as the head-end treatment. An objective of the current investigation was the establishment of the optimum conditions of this treatment by using the data (a) from the exploratory work on HF-promoted destructive oxidation of stainless steel in the absence of fluid beds at ORNL,²⁵ (b) from the development work on the solid-fluoride-promoted destructive oxidation of stainless steel in fluid beds of alumina at BNL,²⁴ (c) from the extensive work on the corrosion rates of Nickel-200 in HF atmospheres available in literature,²⁸ and (d) from the appropriate studies on the destructive oxidation of stainless steel in the presence of fluid beds of alumina at ANL. The studies on the destructive oxidation of (1) SS rods, (2) SS tubes packed with UO_2 pellets, and (3) UO_2 -SS fuels, conducted at ANL to achieve this objective are discussed in paragraphs 1-3 below. In all these tests, the composition of the feed gas to the fluid-bed reactor was 40 v/o HF, 40 v/o oxygen, and 20 v/o nitrogen, found to produce high penetration rates in the exploratory work at ORNL.

1. Destructive Oxidation of Stainless-steel Rods

Four tests were made with fluid-bed temperatures of 500 to 600°C to determine the optimum bed temperature for the oxidation. Type 304 SS rods, 1/2 in. diam and 23 in. long, were used as the test specimens, and sintered alumina, manufactured by Alcoa, was used as the inert fluid-bed material (for details, see Table XIV).

The penetration rates increased with temperature from ~2 mils/hr at 500°C to ~33 mils/hr at 600°C. A practical operating temperature was about 550°C, which gave a penetration rate of about 30 mils/hr. Penetration was markedly higher for the portion of the specimen immersed in the fluid bed than for that above the bed, as shown in Fig. 4; also, in the fluid bed itself, the rates were highest at the bottom of the specimen that

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Fig. 4. Penetration Rates of Type 304 Stainless-steel Rod Immersed in a Fluid Bed When Exposed to Hydrogen Fluoride-Oxygen at 550°C

Initial dimensions: 1/2-in.-diam, 23-in.-long rod
 Initial weight: 583.9 g
 Final weight: 392.4 g
 Run time: 3 hr
 Composition of feed gas: 40 v/o HF, 40 v/o oxygen, 20 v/o nitrogen
 Fluid-bed material: Sintered alumina

to U_3O_8 , indicating that satisfactory exposure of the UO_2 dispersed in stainless steel might occur as a consequence of this head-end treatment, and the uranium may be recovered by subsequent fluorination.

was contacted by the entering gases and decreased in the direction of gas flow. This treatment with HF-oxygen mixture converted the stainless steel to scales containing $\alpha\text{-Fe}_2\text{O}_3$ as the major constituent and Fe_3O_4 as a minor constituent.

2. Stainless-steel Tubes Packed with Uranium Dioxide Pellets

Before the runs with UO_2 -SS fuels, a run (Run HF-1, Table XIV) was made with a 1/2-in.-OD SS tube packed with UO_2 pellets to ascertain the behavior of stainless steel and UO_2 in their mutual presence.

The SS cladding on the pellets was completely destroyed, and the ferric oxide scales disintegrated; the exfoliation of the cladding oxides surrounding the pellets is shown in Fig. 5. The peripheral surface of UO_2 pellets was oxidized

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Note the exfoliation of the outer ferric oxide scales.

Fig. 5. Top and Side Views of Uranium Dioxide Pellets Clad with Type 304 Stainless Steel after 3-hr Exposure to Hydrogen Fluoride and Oxygen at 600°C
(1/16-in. Divisions on Scale)

3. Uranium Dioxide-Stainless Steel Cermet Fuels

Miniature fuel-element subassemblies, simulating those used in the stationary medium-power plants,³ were processed in three runs. Each miniature subassembly consisted of four plates and weighed 90 g; each plate was composed of 18 w/o UO₂-stainless steel (Type 304) cermet, clad in stainless steel. The fuel was decladded in fluid beds of alumina maintained at 550°C in 3 to 6 hr (see Table XV for details).

The subassemblies were completely disintegrated at the end of the destructive oxidation period. The screen analysis of the beds at this stage in a run are given in Table IV. The mixed bed was fluidizable.

TABLE IV. Screen Analyses of Reactor Bed
before and after Destructive Oxidation of
Uranium Dioxide-Stainless Steel
Cermet Fuel

U. S. Sieve Size	Percent of Reactor Bed	
	Before Oxidation	After Oxidation
+45	0.1	24.8
-45 +100	91.6	62.0
-100 +325	8.3	12.6
-325	-	0.6

V. THE FLUORINATION STEP

The alumina beds (both in the fluid- and filter-bed sections), containing the uranium compounds after the separation step, are contacted with fluorine to recover the uranium as the hexafluoride. The bed material, after one or more process cycles, is discarded because of the buildup of (a) heat and radioactivity from the accumulation of fission products, and (b) nonvolatile fluoride matrix and fission-product fines; therefore any uranium associated with this waste bed is a loss. An objective of the current studies was to establish fluorination conditions that would result in minimal amounts of this uranium loss.

A. Effect of Fluorination Procedure on the Recovery of Uranium from Alumina

Of the five fluorination procedures evaluated with the U-Zr fuels (ANL-6829, p. 37), the two most promising procedures, which resulted in very low uranium losses, were tested in the current work. The difference between the two procedures is in the rate at which fluorine is fed to the reactor during the final cleanup period. In one case, the flow rates were more than sufficient to fluidize the alumina bed in the reactor, whereas in the second case they were not.

The results of a fluid-bed fluorination of the alumina in the reactor section are illustrated in Fig. 6 and given in Table V for a typical run with U-Al fuels. In this run, the fluorine concentration was gradually increased from 5 to 90 v/o (approximately 10 v/o every 10 min) during the initial $1\frac{1}{2}$ hr of 2-hr periods at 250 and 500°C. During each period, an increase in the fluorine concentration reduced the uranium concentration in the alumina, from 0.7 to 0.01 w/o at 250°C in the first period, and from 0.01 to 0.003 w/o at 500°C in the second period.

Fig. 6. Uranium Concentrations in the Alumina of Fluid-bed Section during Fluorination. Effects of fluorine concentration, time, and temperature on uranium concentration in the alumina of the fluid-bed section. Reaction cycle: Hydrochlorination-hydrofluorination-fluorination; Reaction bed: 320 g of fused alumina, -80 +100 mesh (see Table V for run conditions).

TABLE V. Uranium Concentration in the Alumina of the Fluid-bed Section during Fluorination

Fuel charge: 165 g of 4.2 w/o uranium-aluminum alloy fuel
 Reaction cycle: Hydrochlorination-hydrofluorination-fluorination
 Reaction bed: 320 g of fused alumina -80 +100 mesh
 (see Tables XII and XIII, Run Al-2, for additional details)

Fluorination Time, hr	Temperature, °C	Quantity, Stoichiometric Amounts ^a	Maximum Concentration of Fluorine, v/o ^b	Residual Uranium in Alumina, w/o
0.5	250	15	20	0.2
1.0	250	52	50	0.03
1.5	250	91	80	0.015
2.0	250	117	90	0.01
2.5	500	15	20	<0.01 ^c
3.0	500	52	50	<0.01 ^c
3.5	500	91	80	<0.01 ^c
4.0	500	117	90	0.003

^aStoichiometric amount to fluorinate 0.1 g of UF₄ to UF₆.

^bConcentration of fluorine is increased in steps of 10 v/o every 10 min to the values indicated above.

^cAnalysis by X-ray spectrographic method. More accurate analysis was not obtained.

During the cleanup period at 500 to 550°C, low flow rates of fluorine (at 1/10th the minimum fluidization velocity), reduced the final concentration of uranium in the reactor-bed material to the same low levels as high flow rates, at three times the minimum fluidization velocity, while both types of fuels were being processed. Results from a typical

run with UO₂-SS fuel, illustrated in Fig. 7 and Table VI, indicate that the concentration of uranium in the bed, containing nonvolatile compounds of the stainless-steel components in addition to the compounds of uranium, was reduced from 0.16 to 0.005 w/o in 8 hr. In this run, the reactor bed was maintained static during the final 2 hr of the fluorination at 550°C.

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Fig. 7. Effects of Fluorine Concentration, Time, and Temperature on Uranium Concentration in the Reactor-bed Material. For additional details, see Table XV, Run HF-13.

The quantity of uranium retained by the bed material in the fluid-bed reactor at the end of fluorination was unaffected by the presence of relatively large amounts of the reaction products of either the stainless steel or the fission products; e.g., in three typical runs, the residual uranium concentrations were 0.005, 0.01, and 0.005 w/o, respectively, when UO₂-SS fuel, U-Al fuel along with fission products, and U-Al fuel alone were processed.

TABLE VI. Effects of Fluorine Concentration, Time, and Temperature on Uranium Concentration in the Reactor-bed Material

Fuel charge: 90 g UO_2 -SS fuel-element subassembly;
 type of stainless steel: 304;
 uranium in the fuel charge: 3.64 g.

Destructive
 oxidation Temperature: 550°C; for additional details,
 see Table XV, Run HF-13.

Fluorination Time, hr	Temperature, °C	Maximum Concentration of Fluorine, v/o	Residual Uranium in Reactor-bed Material, w/o
0	250	4	0.160
1	250	4	0.031
2	250	3	0.062
3	250	7	0.035
4	250	14	0.017
5	250	35	0.015
6	250	56	0.012
7	400	66	0.008
8	520	63	0.011
9	525	85	0.005
10	550	95	0.004
11	550	95	0.008

Nonrecoverable uranium associated with the alumina at the end of fluorination was at a low level, <1% of that in the initial charge, regardless of the moisture content (<1100 ppm) of HCl or the type of alumina used

B. Overall Analysis of the Effect of Operating Conditions on Uranium Retained by Alumina at the End of Fluorination

Uranium retained by alumina after fluorination is believed to be affected by all the process operating conditions, including those of the steps before fluorination (hydrochlorination and hydrofluorination for alloy fuels and reaction with HF-oxygen for cermet fuels). The effects of 19 variables were evaluated by using a stepwise regression analysis²⁹ of the data from both U-Zr and U-Al work; included in the analysis were such items as reaction temperatures, mass velocities, size and type of alumina, and the partial pressure of UF_6 produced during fluorination.

Two computer programs for stepwise multiple-regression analysis, ERMPR 2 by Esso Research and Engineering³⁰ and BIMD 34 by the University of California,³¹ were used in the current study; the first, to scan the data

and establish general trends, and the second, to obtain the regression coefficients in the nonlinear equations. These programs calculated multiple regression in a stepwise manner; i.e., at each step a variable was added to the regression equation which made the greatest improvement in "goodness of fit."

The 19 operating conditions and their partial correlation coefficients are listed in Table VII in the order of decreasing absolute values of the coefficients. Results of this analysis, which involved 41 sets of experimental data from alloy-fuel experiments, indicate that those conditions that tended to decrease the partial pressure of UF_6 in the gas stream resulted in lower retention of uranium by alumina. For example, lowering of the temperature to $250^\circ C$ during fluorination resulted in lower fluorination rates and hence lower partial pressures of UF_6 . Specific hydrochlorination conditions may also have produced such an effect: a form of uranium chloride that reacts slowly with fluorine may have been produced during a particular hydrochlorination; slow reaction of this material during fluorination results in low UF_6 partial pressures in the gas stream. Further, the analysis showed that lower temperatures of the fluid

TABLE VII. Effects of Hydrochlorination and Fluorination Conditions on Uranium Retained by Alumina at End of Fluorination

The concentration of uranium in alumina at the end of fluorination decreased with:	
	Partial Correlation Coefficient
1. Decrease in average rate (based on thermal-conductivity cell observations) of uranium recovery during initial part of fluorination	0.83
2. Decrease in temperature during initial part of fluorination	0.67
3. Decrease in average hydrochlorination rate of uranium based on total time	0.63
4. Decrease in temperature during hydrochlorination	0.55
5. Decrease in mass velocity during hydrochlorination	0.53
6. Decrease in mass of uranium processed	0.52
7. Decrease in mass velocity during fluorination	0.49
8. Increase in temperature during final part of fluorination	-0.41
9. Decrease in average rate of uranium recovery based on total time	0.38
10. Decrease in maximum temperature reached by fluid bed during hydrochlorination	0.34
11. Decrease in maximum temperature reached by bed during temperature excursion while bed was being fluorinated	0.33
The following variables either have insignificant effects, or their values were not sufficiently changed to estimate their effects reliably:	
12. Decrease in average mesh size of alumina	0.31
13. Decrease in average rate of hydrochlorination based on hydrogen production	0.31
14. Increase in maximum partial pressure of HCl in the reactor	-0.27
15. Decrease in average partial pressure of HCl during entire hydrochlorination	0.18
16. Decrease in average rate of uranium recovery based on time for low-temperature fluorination	0.14
17. Decrease in w/o of zirconium in alumina	0.08
18. Decrease in stoichiometric amounts of HCl	0.04
19. Increase in fuel temperature during hydrochlorination	-0.02

bed and lower mass velocities of the gas stream resulted in lower retention of uranium by alumina, and the effects of fluorination conditions are more significant than those of hydrochlorination conditions.

C. Semiempirical Correlation for Uranium Retained by Alumina

In further data-analysis work, a semiempirical relation for possible scale-up application was determined from the experimental data on the concentration of uranium in alumina beds at the end of fluorination. The w/o of uranium, W , in the alumina bed was represented by the following equation:

$$W = 0.0000573 \frac{tp_{\text{UF}_6}^{1.78} \exp(123.8/T)}{r^{0.56} p_{\text{F}_2}^{0.7}}, \quad (1)$$

where t is the time during which 90% of the uranium in the fuel charge is recovered; p_{UF_6} is the average partial pressure of UF_6 in the bed during time t ; T is the temperature of the bed during the final high-temperature stage of fluorination; r is the rate of uranium recovery based on total fluorination time; and p_{F_2} is the maximum partial pressure of fluorine to which the alumina was exposed. The proposed relationship is applicable for concentrations of residual uranium in the range of 0.002 to 0.06 w/o and in the following ranges for the operating conditions:

t : from 0.2 to 4.0 hr,

p_{UF_6} : from 1.1 to 22 mm Hg,

T : from 623 to 773°K,

r : from 0.0016 to 0.028 kg of uranium per hr per kg of alumina,

p_{F_2} : from 0.6 to 1.2 atm.

A total of 41 sets of experimental data on uranium retained by alumina in the fluid bed as well as in the packed-bed filter were represented by this relation with an average error of $\pm 40\%$, which is considered satisfactory for design purposes. The experimental values of uranium concentration in alumina, and those calculated from Equation (1), are given in Table VIII.

TABLE VIII. Experimental and Calculated Values of Concentration of Uranium Retained by Alumina

Run Number ^a	Average Rate of Uranium Recovery Based on Total Time, kg of U/(hr) (kg of alumina)	Maximum P_{F_2} , atm	Temperature of Bed during High-temperature Fluorination, °C	P_{UF_6} , mm Hg	Concentration of Uranium Retained by Alumina, w/o	
					Experimental	Calculated
Bench-scale Development with Normal Uranium-alloy Fuels (Data were used in obtaining the correlation)						
23F	0.0054	0.86	350	16.9	0.061	0.054
19F	0.0051	0.99	350	22.3	0.060	0.084
31F	0.0097	1.02	500	15.5	0.050	0.025
24F	0.0054	0.98	550	14.1	0.050	0.041
35F	0.0281	0.86	500	10.9	0.050	0.035
23P	0.0094	0.80	350	14.8	0.045	0.033
29F	0.0225	0.84	500	9.7	0.040	0.012
20F	0.0051	1.16	350	13.4	0.033	0.051
24P	0.0094	0.93	550	12.3	0.031	0.024
26F	0.0044	1.07	500	9.0	0.030	0.016
25F	0.0075	0.82	500	12.2	0.030	0.033
27F	0.0044	0.88	500	6.8	0.030	0.020
34F	0.0169	0.64	500	9.1	0.030	0.037
32P	0.0284	0.68	500	8.5	0.029	0.029
19P	0.0074	0.93	350	18.6	0.026	0.051
32F	0.0284	0.70	500	9.9	0.025	0.037
20P	0.0076	1.10	350	11.2	0.021	0.030
30P	0.0084	0.78	500	7.6	0.020	0.028
34P	0.0169	0.60	500	7.7	0.017	0.018
28F	0.0034	0.88	500	5.0	0.017	0.018
40P	0.0069	1.12	510	3.8	0.016	0.014
35P	0.0281	0.84	500	9.3	0.015	0.027
31P	0.0097	0.98	500	13.3	0.014	0.020
40F	0.0069	1.16	540	4.7	0.013	0.022
30P	0.0084	0.74	500	6.1	0.013	0.020
39F	0.0081	0.90	500	5.0	0.012	0.011
4P	0.0028	0.90	485	1.1	0.011	0.003
37F	0.0016	0.81	500	4.6	0.010	0.011
38F	0.0038	1.08	500	4.9	0.010	0.010
4F	0.0030	1.14	495	1.4	0.010	0.004
41F	0.0060	1.14	540	4.7	0.008	0.010
37P	0.0016	0.78	500	3.8	0.007	0.008
41P	0.0060	0.90	490	3.8	0.006	0.005
39P	0.0081	0.84	500	3.8	0.006	0.007
38P	0.0038	0.98	500	3.7	0.004	0.007
3F	0.0072	1.04	500	2.8	0.004	0.008
3P	0.0072	1.02	500	2.1	0.003	0.005
2F	0.0053	1.14	500	1.6	0.003	0.004
2P	0.0053	1.10	500	1.2	0.002	0.003
Bench-scale Development with Irradiated Uranium-alloy Fuels ²⁰ (Data were not used in obtaining the correlation)						
SCIZ-1F	0.0030	0.7	540	4.7	0.005	0.002
SCIZ-2F	0.0028	0.88	525	4.2	0.005	0.002
SCIZ-1P	0.0058	0.7	510	4.7	0.005	0.001
SCIZ-2P	0.0054	0.88	510	4.2	0.002	0.001
SCAZ-1F	0.0017	0.84	510	2.6	0.006	0.001
SCAZ-2F	0.0015	0.84	510	2.4	0.007	0.001
SCAZ-1P	0.0013	0.84	485	2.6	0.002	0.001
SCAZ-2P	0.0012	0.84	473	2.4	0.002	0.001
SCIA-1F	0.0023	0.94	520	4.3	0.002	0.001
SCIA-2F	0.0023	0.83	515	3.7	0.001	0.001
SCIA-1P	0.0019	0.94	500	4.3	0.001	0.001
SCIA-2P	0.0019	0.83	495	3.7	0.001	0.001
Pilot-scale Development with Normal Uranium-alloy Fuels ¹⁹ (Data were not used in obtaining the correlation)						
9F	0.0047	1.22	500	17.0	0.002	0.018
10F	0.0094	1.12	500	5.0	0.011	0.103
10P	0.0239	1.12	500	5.0	0.04	0.062
9P	0.0159	1.22	500	17.0	0.021	0.350
12P	0.0052	1.25	500	4.3	0.005	0.001
8F	0.0063	2.25	500	3.5	0.001	0.001
7F	0.0045	1.18	500	2.4	0.004	0.001
7P	0.0178	1.18	500	2.4	0.009	0.001
8P	0.0361	2.25	500	3.5	0.03	0.001
12P	0.0184	1.25	500	4.3	0.002	0.001

^aF represents alumina in the fluid-bed reactor; P represents alumina in the packed-bed filter.

The values predicted by the use of the equation for fluorination in a 6-in.-diam fluid-bed reactor (pilot-scale operation), and for fluorination in a $1\frac{1}{2}$ -in.-diam fluid-bed reactor (bench-scale operation) with irradiated fuels, agreed, within the error, with those determined experimentally (see Table VIII), although the predictions were made using the values of operating conditions beyond those proposed for the correlation. Only when a run was not operated satisfactorily is there a wide disagreement between the predicted and experimental values. For example, the experimental values, 0.002 and 0.021 w/o, are more than an order of magnitude less than those predicted, 0.18 and 0.35 w/o, in a pilot-scale run (Run 9) during which the packed-bed filter caked. Similarly, the experimental values, 0.027 and 0.041 w/o, are more than an order of magnitude greater than those predicted, 0.002 and 0.002 w/o, for a bench-scale run (Run SCIZ-4) in which the U-Zr fuel was incompletely hydrochlorinated. These observations point out the usefulness of the proposed correlation for performance check on future run operations.

VI. OVERALL PROCESS CONSIDERATIONS

Economic operation of the process equipment requires data on the distributions of uranium, fission products, and cladding constituents in various process streams, in addition to information on the operating conditions for the separation and fluorination steps. Also, the performance of the packed-bed filter and the behavior of the alumina during the reaction cycles are of interest from process scale-up considerations. These, along with the corrosion rates of Nickel-200 in the process environments, are discussed in this section.

A. Uranium Distribution

Results of uranium distributions for one run each with the U-Al and UO_2 -SS fuels are given in Table IX.

TABLE IX. Uranium Distribution in Process Streams
(For run operating conditions, see appendix.)

<u>Run No.</u>	<u>Al-3</u>	<u>HF-16</u>
Type of fuel subassembly	U-Al	UO_2 -SS Cermet
Fuel charge, g	172	90
Uranium in the fuel charge, g	8.9	5.3
<u>Uranium Recovered</u>	<u>% of Uranium in the Charge</u>	
1. UF_6 product recovered from cold traps	99.0	80.9
2. UF_6 recovered from activated alumina traps	0.1	17.4
3. Uranium in bed samples	<u>0.6</u>	<u>0.9</u>
Total uranium recovered	99.7	99.2
<u>Uranium Lost</u>		
1. Uranium retained in alumina		
a. In fluid bed	0.1	0.8
b. In packed-bed filter	0.1	-
2. Uranium loss through packed-bed filter during hydrochlorination	0.1	-

For the run with U-Al fuel, the uranium recovered was 99.7% of that in the initial fuel charge. The uranium losses were only 0.1% due to that passed through the packed-bed filter during hydrochlorination, and 0.1% each due to that retained by the alumina in the fluid and filter beds at the end of fluorination.

Similarly, for the run with UO_2 -SS fuel, of the 5.3 g of uranium in the initial fuel charge, only 0.04 g or 0.8% was associated with the fluid bed at the end of fluorination, and may be considered as a loss.

B. Distribution of Fission Products and Alloying Constituents of the Cladding

Some of the fission products and/or some of the cladding constituents volatilize during the two process steps. Data on the disposition of these elements is important to the design of the uranium hexafluoride purification system, the aluminum chloride pyrohydrolysis equipment used during the hydrochlorination of U-Al fuels, and the solid-waste storage system.

To obtain such data, a mixture of inactive fission-product elements was processed along with the U-Al fuel in one of the runs. The composition of the fission-product mixture was similar to that calculated by Burris and Dillon³² for U^{235} for 150 days irradiation and 30 days cooling; 11 fission-product elements* with concentration greater than that of antimony (0.027 g of antimony per 100 g of U^{235}) and with specific activity greater than that of molybdenum (2.3 Ci/g) were represented; lanthanum and rare-earth elements, except cerium, were not added. The total weight of the added fission products was 13.7 g, equivalent to 4.2 w/o of the alumina in the fluid bed. The fates of these elements were ascertained by X-ray spectrographic and spectrochemical analyses of the samples from various process streams.

The relative distributions of most of the fission products conformed with the distributions estimated from the volatilities of their higher-valent chlorides and fluorides, and are similar to those presented in the companion report on the bench-scale development of the FBV process for U-Zr fuels (ANL-6829, p. 42). Barium, cerium, cesium, strontium, and yttrium remained with the alumina in the fluid and filter beds; molybdenum, niobium, and ruthenium were distributed among the volatile chloride condenser, the UF_6 cold traps, and the reactor; and rhodium, antimony, and tellurium could not be detected because of the insensitivity of the analyses. Although appreciable information is now available on the distribution of these elements, work with irradiated fuel sections is in progress to confirm and refine these data.

Since the U-Al fuel elements contain silicon from the brazing alloy used during their manufacture⁴ and from aluminum transmutation to silicon during irradiation,³³ the behavior of silicon during the two processing steps was established. Silicon, contrary to the behavior of fission products mentioned in the above paragraph, was retained mainly in the reactor system during the hydrochlorination; a minor amount, <5% of the silicon in the charge, was collected with the UF_6 product during the fluorination.

*Strontium, yttrium, niobium, molybdenum, ruthenium, rhodium, antimony, tellurium, cesium, barium, and cerium.

The material balances for iron and chromium were determined for all the runs with the UO_2 -SS fuels from the results of spectrochemical and wet-chemical analyses of samples from various process streams. During the destructive oxidation, iron and chromium did not volatilize in detectable quantities. However, during fluorination, some chromium volatilized, and the rate of volatilization increased with increase in temperature and fluorine concentration. In all the runs, less than 50% of the chromium in the fuel charge volatilized, the iron being totally retained in the reactor system. The iron and chromium compounds remaining in the reactor were transformed to very fine particulate fluorides by the end of fluorination.

C. Performance of the Packed-bed Filter during the Processing of Uranium-Aluminum Alloy Fuels

During the head-end step for the highly-enriched uranium fuels, the uranium is separated from the cladding in fluidized beds of alumina by the formation of particulate compounds, and a minor portion of the particulate uranium compounds is entrained by the gas stream exiting the fluidized bed. For economic reasons, these uranium compounds in the gas stream should be retained in the reactor system and be made available for recovery by fluorination.

A high-temperature gas filter is needed to retain the particulate uranium compounds in the reactor system. This filter will be exposed to excess HCl , nitrogen, hydrogen, and aluminum chloride at temperatures of 180 to 200°C while U-Al fuels are being processed, and to excess HF and oxygen at 50 to 100°C while UO_2 -SS fuels are being processed. The filter has to be maintained at these temperature levels to prevent the condensation of the volatile materials, viz., aluminum chloride for the U-Al fuels, and HF for the UO_2 -SS fuels. Any filter, such as a packed-bed filter or a sintered-nickel filter, that can perform satisfactorily in these process environments could be used to retain uranium during the separation step.

To prevent the condensation of volatile ZrCl_4 (sublimation point 331°C, 1 atm) while U-Zr fuels are being processed, the filter has to be maintained at relatively higher temperatures, 330 to 350°C; and early in the bench-scale development of the FBV process for U-Zr fuels, packed beds of alumina were found to be satisfactory as filters. After this phase of process development for the U-Zr fuels, the development of the process for U-Al fuel was initiated; subsequently, the runs for the development of the process for both the fuels were conducted alternately. Therefore the packed-bed filter was used for simplicity with U-Al runs although a sintered-nickel filter, which is satisfactory at the lower temperatures, could have been used for these runs. Also, for uniformity in process equipment, the packed beds of alumina could be used as filters while the three types of fuels were being processed. For this reason, the performance of the packed-bed filter is of interest.

The optimum depth for the packed-bed filter may be defined as the depth that results in lowest total uranium loss due to its use. The loss is due to the two sources: the uranium contained in the gas stream exiting the filter during hydrochlorination, and the uranium retained by alumina at the end of the fluorination step. The former loss decreases with bed depth (see Table II and Fig. 2); the latter increases with depth due to increase in the quantity of alumina. Both these losses approach equilibrium values with increase in depth (see Fig. 8). Based on the experimental data in the runs

Fig. 8. Determination of the Optimum Depth of Packed-bed Filter

with U-Al fuel, the optimum bed depth appears to be about 9 in. for lowest total uranium loss. This method of determining the optimum bed depth is illustrated to facilitate the design of large-scale filters; also of help in the design of large-scale filters is the knowledge of pressure drop for flow of gases (ANL-6829, p. 46).

D. The Behavior of Alumina

High-fired alumina (both fused and sintered types) was found to be a satisfactory inert bed material. Its stability as regards caking tendencies was tested in a group of atypical experiments in which planned interruptions were carried out during and after each reaction step of the processing cycle. During the reaction steps, the interruptions consisted of (a) stopping the gas flow, causing the fluid bed to become static, (b) rapidly cooling the reactor from its operating temperature to room temperature, (c) maintaining the reactor at room temperature for 2 hr, and (d) reheating the reactor to the operating temperature. Planned interruptions after a reaction step involved (a) stopping the gas flow, (b) heating the reactor assembly (fluid-bed reactor and packed-bed filter) to 600°C, (c) maintaining the assembly at this temperature for 2 hr, and (d) cooling the assembly from 600°C to the normal operating temperature.

The alumina in the fluid bed did not cake or agglomerate during any of the interruptions; the alumina was readily refluidized upon startup of the gas flow and also drained readily from the reactor after the experiment was completed. No caking occurred in the alumina packed-bed filter, and it, too, drained freely.

By the end of a reaction sequence, alumina particles were coated with solid reaction products whose chemical structure was not identified; further, some alumina attrited. But these changes did not affect the overall column operation and the results.

E. Corrosion

Nickel is considered as the likely material of construction for the FBV process equipment. Consequently, information on corrosion of nickel was obtained from specimens mounted in the fluid-bed and disengaging zones during some of the runs in the current work.

The corrosion specimens were exposed to HF and oxygen mixtures at about 550°C for 21 hr in six runs, thermal cycling between room temperature and the operating temperature being interposed between the runs. The average corrosion rates were 8.8 and 17.5 mils/yr, respectively, for specimens in the disengaging chamber and the fluid-bed reactor section.

Previous studies on the corrosion of nickel in FBV process environments³⁴ pointed out that the corrosion rates were less than 30 to 40 mils/yr, while uranium-alloy fuels were being processed and no intergranular attack was noticed. These and the above data indicate that nickel will be satisfactory as a material of construction.

VII. CONCLUSIONS

With the completion of the current development studies, the FBV process has been shown to be applicable to the most commonly-used, highly-enriched, uranium fuels. High recoveries of uranium, greater than 99% of that in the charge, have been consistently achieved with the U-Al and UO_2 -SS fuels. Similar high recoveries of uranium from U-Zr fuels were reported in a previous development study (ANL-6829).

The development studies, conducted in a $1\frac{1}{2}$ -in.-diam nickel fluid-bed reactor system, established processing conditions for all three types of fuels. The process consists of a separation step, in which the uranium is freed from its cladding, and a recovery step, in which the uranium thus freed is recovered, by fluorination, as the hexafluoride. Most of the operating conditions for processing the three types of fuels are similar, except for the reagents and temperatures used during the separation step, and a wide choice in the processing conditions is available.

Considerable economic advantage of this FBV process over the aqueous processes currently used for the recovery of uranium from highly-enriched uranium fuels appears possible because the FBV process (1) involves fewer and simpler operations, (2) results in smaller volumes of high-level radioactive solid wastes with fewer disposal problems, and (3) produces UF_6 , which is readily amenable to isotope separation and/or reconversion as fuel. Thus, process scale-up to full-scale plant appears very promising.

APPENDIX

Supplementary InformationA. Analyses of Gases and Inert Bed Materials

Commercial-grade chemicals were used throughout the current process-development work. The typical compositions of commercial-grade gases are given in Table X. The types of alumina used as inert bed material in the current work are described in Table XI.

TABLE X. Compositions of Commercial-grade Gases Used in Current Work

Gas	Name of Manufacturer	Composition Guaranteed by Manufacturer		
		Minimum Concentration of Main Gas. v o	Typical Impurities	
			Gas	Maximum Concentration. v o
N ₂	Air Products and Chemicals	99.997	O ₂	0.003
HCl	Matheson Co.	99.0	Air	0.2
			CO ₂	0.5
			H ₂ O	30 ppm
			SO ₂	} ~0.3
			C ₆ H ₆	
			Unidentified compounds	
H ₂	Liquid Carbonic	99.95	N ₂	40 ppm
			O ₂	1 ppm
			CO	60 ppm
			CO ₂	8 ppm
			CH ₄ , etc.	100 ppm
			H ₂ O	35 ppm
F ₂	General Chemical Division Allied Chemical and Dye Corp.	98.5	O ₂	0.2
			N ₂	0.7
			CF ₄	} 0.5
			SiF ₄	
			CO ₂	
Standard gas mixtures of N ₂ + H ₂ and N ₂ + Cl ₂	Matheson Co.		O ₂	0.2
HF	Harshaw Chemical Co.	99.96	SiF ₄	0.006
			SO ₂	0.007
			H ₂ O	0.019
			H ₂ SO ₄ + HFSO ₃	0.005
O ₂	General Dynamics Corp.	99.5	N ₂	} ~0.5
			A	
			H ₂ O	
				<11 ppm

TABLE XI. Properties of the Aluminas Used in Bed Materials

Constituent,	Fused Alumina (Alundum ^a)		Sintered Alumina, Tabular, Type T-61 ^b
	Type RR (Blue Label)	Type 38	
Al ₂ O ₃ , w/o	99.5+	99.49	99.5+
SiO ₂ , w/o	<0.01	0.05	0.06
Fe ₂ O ₃ , w/o	0.03	0.10	0.06
Na ₂ O, w/o	<0.02	0.35	0.03
Uranium, w/o	0.0003	0.0005 to 0.0009	0.0004
Property			
Bulk density, packed, lb/cu ft	116	116	135
True density, g/ml	3.96	3.96	3.96
Specific gravity	3.89	3.87	3.65 to 3.8
Hardness (Mohs Scale)	Not available	9	9
Melting point, °C	2000	2000	2040
Cost ^c , c/lb	69	33	14

^aManufactured by Norton Company, Worcester 6, Massachusetts.

^bManufactured by Aluminum Company of America, Bauxite, Arkansas.

^cCosts based on 100-lb lots.

B. Summary of Experimental Data

The experimental data obtained in this investigation on the processing of U-Al fuels are summarized chronologically in Tables XII and XIII, those on the destructive oxidation of stainless steel in Table XIV, and those on the processing of UO₂-SS fuels in Table XV.

TABLE XII. Data on Runs with Uranium-Aluminum Alloy Fuels: Fuel and Alumina Charges to the Reactor System

Run No.	Fuel Charge ^a							Alumina Charge					
	Wt, g	Concentration of U, w/o ^b	No. of Subassemblies	No. of Plates	Plate Width, in.	Plate Length, in.	Plate Spacing, in.	Reaction Bed			Packed Bed		
								Wt, g	Mesh Size	Type	Wt, g	Mesh Size	Type
Al-1	240 97 unreacted 143	3.1	None		0.12	0.4		320	-40 +60	RR ^c	320	29 ^d	38 ^c
Al-2	165	4.2	3	5	0.78	5	0.05 ^d	320	-80 +100	38 ^c	320	-14 +20	38 ^c
Al-3	172	5.2	3	5	0.78	5	0.05 ^d	320	-40 +120	T-61 ^e	430	-14 +20	T-61 ^e
Al-4	176.7 ^f	3.9	4	3	0.78	5	0.05 ^g	320	-40 +120	T-61 ^e	640	-14 +20	T-61 ^e
				4	0.78	5							
				2	0.78	5							
				5	0.78	5							
Al-5	188.5	3.9	4	3	0.78	5	0.1 ^g	320	-40 -120	T-61 ^e	534	-14 +20	T-61 ^e

^aThe fuel charge comprised normal uranium-aluminum alloy clad with aluminum; the fuel plates were ~0.05 in. thick.

^bAccounted by the method discussed previously (ANL-6829, p. 42).

^cFused alumina manufactured by Norton Company.

^dPlates were brazed together with Al-1100 rods, containing >99% aluminum, manufactured by Eutectic Welding Alloys Corporation.

^eSintered alumina manufactured by Aluminum Company of America.

^fFission products, 13.7 g, were charged with the fuel.

^gPlates were brazed together with Castolin rods, containing 12 w/o silicon, manufactured by Eutectic Welding Alloys Corporation.

TABLE XIII. Data on Runs with Uranium-Aluminum Alloy Fuels: Operating Conditions and Results during the Separation and Fluorination Steps
Fluidizing gas velocity: ~0.5 to 0.6 ft/sec at column conditions

Run No.	Separation Step								Fluorination Step					
	Hydrochlorination						Hydrofluorination			Max Fluorine Partial Pressure, atm	Residual U Content of Alumina, w/o			
	Time, hr	Av Fluid-bed Temp, °C	Av Packed-bed Filter Temp, °C	HCl Quantity X Stoichiometric	U Loss, %	Time, hr					Temp, °C	Feed Concentration, v/o	Time, hr	Temp, °C
Al-1	3.25	375	230	0.6	2.5	None				1.5	350			
Al-2	2.5	~290	215	1.1 ^b i	1.2	1.0	200	50	2.0	250	1.1	0.003	0.0016	
	5.0	~250	205	2.5 ^c j		1.0	275	50	2.0	500				
						1.0	350	50						
Al-3	3.3	230	185	1.4 ^c k	0.1	1.0	350	50	2.0	250	1.0	0.0039	0.0029	
	4.2	220	200	1.6 ^b l					2.0	500				
Al-4	1.5	200	200	Fission product only		1.0	350	52	6.0	250	1.2	0.01	0.011	
	1.2	380	160	0.4	0.1				2.4	250				
	5.2	290	170	2.1					6.0	500				
Al-5	7.0	250	225	2.3	0.27	1.0	352	34	2.0	250 to 500	1.00	0.005 ^e	0.004 ^e	
									2.0 ^d	500				

^aPacked bed of alumina was drained for examination after hydrochlorination.

^bOne subassembly was hydrochlorinated.

^cTwo subassemblies were hydrochlorinated.

^dDuring this period, the gas velocity was ~0.01 ft/sec at column conditions, and the alumina in the fluid-bed reactor was static.

^eEqual masses of used alumina from Run Al-3 and fresh alumina were charged to the fluid-bed reactor; used filter-bed alumina, 356 g from Run Al-3 and 178 g from Run Al-2, was charged to the packed-bed filter. Consequently, the uranium concentration is the difference between its final and initial values in the bed.

TABLE XIV. Data on Destructive Oxidation of Stainless Steel in Fluid Beds of Alumina

Stainless-steel rod: Type 304, 1/2 in. diam, 23 in. long
Test Time: 3 hr
Fluidizing-gas velocity: ~0.6 ft/sec at column conditions

	HF-6	HF-7	HF-2	HF-1
Mesh size of granular alumina ^a	48-100	48-100	-30 +50	-30 +50
Feed-gas composition, v/o				
HF	40	40	45	45
Oxygen	40	40	32	32
Nitrogen	20	20	23	23
Temperature of the fluid bed, °C	500	550	550	600
Penetration rates, mils/hr	2	25	30	33

^aSintered alumina, Type T-61, manufactured by Aluminum Company of America.

TABLE XV. Processing of Uranium Dioxide-Stainless Steel Cermet Fuels

Miniature fuel-

element subassembly: Four plates approximately $8\frac{3}{8}$ in. long, $1\frac{1}{16}$ in. wide, 0.03 in. thick were held together at a spacing of $1/8$ in. by a $1/16$ -in.-diam nickel-200 wire.
Weight ~90 g.

Run No.	HF-12	HF-13	HF-16
Number of subassemblies processed	2	1	1
<u>Alumina^a Charged to the Reactor Assembly</u>			
Gas-dispersing medium, g		148	148
Nominal mesh size		-14 +28	-14 +25
Fluid-bed material, g	640	480	480
Nominal mesh size	-48 +100	-48 +100	-45 +100
Packed-bed filter, g	320	320	320
Nominal mesh size	-14 +28	-14 +28	-14 +25
<u>Destructive Oxidation</u>			
Temperature, °C	550	550	550
Time, hr	3	4	6
Feed-gas concentration, v/o			
HF	40	40	40
Oxygen	40	40	40
Nitrogen	20	20	20
Fluidizing-gas velocity, ft/sec	0.6	0.6	0.6
<u>Fluorination</u>			
Temperature, °C	b	250	250
Time, hr		6	5
Feed-gas concentration, v/o			
Fluorine		2 to 90	2 to 90
Nitrogen		98 to 10	98 to 10
Fluidizing-gas velocity, ft/sec		0.6	0.6
Temperature, °C		550 ^c	550 ^c
Time, hr		2 ^d	1 ^d
Feed-gas concentration, v/o			
Fluorine		95	95
Nitrogen		5	5
Fluidizing-gas velocity, ft/sec		0.02	0.02
Total time, hr		11	10.3

^aSintered alumina, Tabular, Type T-61, manufactured by Aluminum Company of America, Bauxite, Arkansas.

^bReactor beds were drained and examined.

^cThe temperature of the reactor assembly was raised gradually from 250 to 550°C while the reactor bed was being fluidized with 90 v/o fluorine in the feed gas stream.

^dDuring this period, the gas velocities in the fluid-bed section were reduced to subfluidizing values, and the reactor-bed material was maintained static.

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