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A PROCESS FOR THE RECOVERY OF URANIUM
FROM NUCLEAR FUEL ELEMENTS
USING FLUID-BED DRYING AND VOLATILITY TECHNIQUES

by

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SUMMARY

A process scheme for the recovery of uranium from a wide variety of nuclear fuel elements has been developed. The scheme combines continuous fluid-bed drying and fluoride volatility techniques after initial dissolution of the fuel element in the appropriate aqueous system, hence the designation ADF, Aqueous Dry Fluorination Process. The work described in this report is the application of this process to the recovery of uranium from highly enriched, low uranium-zirconium alloy plate-type fuels.

In the process, the feed solution is sprayed horizontally through a two-fluid nozzle and is atomized directly in the heated fluidized bed. The spray droplets are dried on the fluidized particles and form a dense coating. Excessive particle growth was limited by the use of air attrition-jets inserted directly in the bed. Aqueous hydrofluoric acid solutions containing 1.2 to 3.6 M zirconium, 0.007 to 0.03 M uranium, and free acid concentrations from 1 to about 10 M were successfully processed in a 6-in.-diameter Inconel fluid-bed spray dryer. Rates equivalent to about 3.1 kg/hr of zirconium were achieved (160 ml/min with the most concentrated feed solution). Experiments were successfully carried out over the temperature range from 240 to 450 C. A new design for a two-fluid nozzle was developed in the course of this work. Extensive work was done to identify the various zirconium fluoride compounds formed.

The granular dryer product was subsequently fluorinated at temperatures to 600 C in fluid beds and to 700 C in static beds to remove the uranium as the volatile hexafluoride. About 90 to 95 percent uranium removal was consistently achieved near 600 C. The relatively low uranium recovery under these conditions is a disadvantage for the application to zirconium-base fuels. It was found necessary to resort to static beds and higher temperatures to achieve greater removal.

Since the fluorine attack on nickel, the material of construction, is prohibitive at temperatures above 600 C, a disposable fluorinator concept for use with static beds is described in Appendix A. Results of corrosion studies are also reported. A preliminary chemical flowsheet with a design capacity of 1100 kg of uranium (93 percent enriched) annually is presented in Appendix B.

Final decontamination of the recovered uranium hexafluoride would be accomplished by fractional distillation. However, the work reported herein included only the investigation of fluid-bed drying and the separation of uranium by fluorination.

I. INTRODUCTION

The increased use of zirconium-bearing fuel elements has prompted studies of processing techniques for recovery of the unburned uranium from the spent fuel. Zirconium has become an important component for a variety of reactor fuel elements because of its low neutron cross section and excellent corrosion resistance. Examples of its use are as cladding in the fuel for the Commonwealth Edison Dresden power reactor - Zircaloy-2-clad* sintered uranium dioxide, or as an alloying agent in the highly enriched, low uranium-Zircaloy-2 plate-type fuel elements. The work described in this report concerns primarily the processing of these plate-type fuels, although the process has more widespread applicability.

Most processes which have been developed, or are now in various stages of development, dissolve or treat the fuel in a manner suitable for recovery of the uranium by solvent extraction.(1-5) In the case of the uranium-Zircaloy alloy fuels, the first step is an aqueous dissolution in hydrofluoric acid. Oxidizing agents are added to effect the dissolution of the tin and to oxidize the uranium from the tetravalent to the hexavalent (more soluble) state.

The objective of the work described here was to develop a process which would recover uranium from the dissolver solution by less expensive, more direct techniques than the solvent extraction method. The process, designated ADF, involves Aqueous dissolution of the uranium-zirconium alloy fuel in hydrofluoric acid, followed by fluid-bed Drying of the dissolver solution, and Fluorination of the dried solids to recover the uranium as uranium hexafluoride. A schematic flow sheet of the ADF process is shown in Figure 1. It may be noted that this scheme may be applied to fuels containing materials other than zirconium merely by choosing the proper acid and materials of construction. An obvious advantage of this process over the solvent extraction technique is that the final waste, containing the majority of the radioactive fission products, is a solid which can be stored and handled more easily than the large volumes of liquid waste which are now produced. This report is divided into two major sections: Fluid-bed Drying and Fluorination Studies, in addition to which there are Appendices on a Disposable Fluorinator Concept and a Preliminary Chemical Flowsheet.

* Zircaloy-2 is a high zirconium alloy currently used in fuel components and contains, in addition to zirconium, 1.5% tin, 0.15% iron, 0.10% chromium, and 0.05% nickel.

FIGURE 1
SCHEMATIC FLOW SHEET FOR THE ADF PROCESS

Fluidization and the Technique of Fluid-bed Drying

The principle of fluidization involves the passage of a gas upwards through a bed of solid particles at a speed sufficiently high to allow the particles to move with a completely random motion within the bed, but not be elutriated from the system. Since the bed of solids possesses a relatively large heat capacity, and the solids move randomly, a fluidized bed provides an attractive means for maintaining a constant-temperature process. The large surface area of the particles available for heat transfer offers an attractive technique for the rapid calcination or drying of salt solutions. Equipment size can be considerably reduced over that of conventional drying equipment. The technique has proved successful in the preparation of uranium trioxide from uranyl nitrate solutions^(6,7) and the calcination of aluminum nitrate radioactive waste solutions.⁽⁸⁾ In both cases the nitrate solute was converted to the oxide in the drying-calcining operation. The deposited material forms as a uniform coating on the individual bed particles. In some instances aggregates (agglomeration of several particles) form. This operation is continuous, and a constant inventory of material is maintained in the calciner by withdrawing product at a rate equivalent to the feed rate.

II. FLUID-BED DRYING

A. Process Equipment and Materials

Equipment included two fluid-bed dryers, the feed makeup and metering system, and the off-gas handling system and auxiliaries as shown schematically in Figure 2. These are discussed in detail below.

FIGURE 2
SCHEMATIC DRAWING OF FLUID-BED DRYING EQUIPMENT

1. Fluid-bed Dryers

The principal reactor used in this investigation was an Inconel column constructed in two separate sections: a 6-in.-diameter by 30-in.-long section which contained the fluidized bed topped by a 12-in.-diameter by 28-in.-long disengaging and filter section. These two sections were joined by flanges. The distributor plate for the fluidizing gas was a bubble-cap type consisting of twelve $\frac{1}{2}$ -in.-diameter tubes capped by $\frac{3}{4}$ -in. flat discs. The gas was admitted through four $\frac{1}{16}$ -in. holes drilled on the periphery of each tube just below the cap. The plate was mounted over a gas-expansion chamber which was an integral part of the lower flange assembly. A 3-in. column of Monel was also used in some of the preliminary studies, but since equipment details were in general similar to those of the larger unit, they will not be described separately.

The starting bed material was charged to the reactor through a $\frac{1}{2}$ -in.-diameter pipe sidearm. Air purges were provided in the line from the solids hopper to the reactor, to obviate solids plugging while the bed was being charged.

The 6-in. column was heated by 30 calrod heaters, each of 100 w, 230 v, wrapped around the column wall. The wall of the reactor was specially grooved to accommodate the heaters. A system of five Variacs was employed to control the power input to the heaters. Four of the Variacs were manually controlled; the fifth was an automatic controller actuated by a thermocouple located in the lower portion of the fluidized bed. The maximum total power supplied to these heaters was approximately 10 kva; the actual power required was dependent primarily on the liquid feed rate. The power input was controlled such that the calrod sheath temperatures measured by thermocouples did not exceed manufacturer's rating (~ 700 C).

Since the throughput of the fluid-bed dryer was limited by the heat transfer area available, additional capacity was provided with an internal heater immersed in the fluidized bed. This heater added approximately 1.8 sq ft of heat transfer surface to the 2.4 sq ft of area provided by the reactor wall, and was an autoresistive type made in the form of two coils, each about 5 in. in OD, from a strip of Inconel, 1 in. wide by $\frac{1}{16}$ -in. thick by 11 ft long. The coils were positioned one above the other and connected by a welded Inconel strap. The coils were inserted into the lower section of the fluidized bed and were connected to a power source (a 300-amp Vickers Controlarc welding machine) by special fittings brought through two spray nozzle ports which were not in use. These ports were located 5.5 in. above the gas-dispersion plate. The power level was generally maintained at 4 kva (17.5 v, 225 amp).

The temperatures of the lower, middle, and upper sections of the bed, three column wall temperatures, inlet temperatures of the pre-heated fluidizing and filter blowback gases, and the gas temperature in the disengaging section were continuously recorded.

Pressure gages were located in the reactor, in the liquid feed line, and in the off-gas line. Also, the pressures of the fluidizing gas, atomizing gas, blowback gas, and attrition air were noted. The flow rates of fluidizing gas, atomizing air, and attrition air were measured by rotameters. The liquid feed rate was measured by weight change of the feed reservoir (a 100-liter polypropylene tank) mounted on a scale, and was metered by a variable-stroke Milton Roy piston pump fitted with a Hastelloy-C head.

The height of the fluidized bed and column pressure were indicated by differential pressure manometers. The column pressure (the differential pressure across the filters) was usually about 4 to 8 in. of mercury.

2. Nozzles

The reactor was constructed with four ports to provide a variety of nozzle arrangements; ports were at $5\frac{1}{2}$ and 11 in. above the gas-distributor plate, two at each elevation. The ports were displaced 90° from each other at each level. The spray nozzles employed during the initial part of this work were two-fluid pneumatic nozzles manufactured by Spraying Systems Company (see Figure 3). The liquid feed is atomized in a high-speed air stream issuing from an annulus which surrounds the liquid nozzle. The high-pressure atomizing air is directed into the annular space (B) by a cap (C) placed around the liquid nozzle (A). Liquid nozzle sizes employed ranged from 0.016 to 0.040 in. in diameter. Atomizing air pressure ranged from 15 to 45 psig, although 30 psig was used for the greatest portion of the work. The nozzles were equipped with cleanout needles, but as the needles were rather fragile and often broke, they were frequently removed and the cleanout port plugged. These nozzles were mounted in the reactor such that the cap protruded about $\frac{1}{16}$ in. from the column wall into the bed. An alternative mounting allowed the nozzle to protrude $\frac{1}{4}$ in. into the fluidized bed. In this case, the retainer ring (D) was removed, the cap welded to the body, and the nozzle machined such that the whole assembly would protrude sufficiently into the bed.

FIGURE 3

SPRAYING SYSTEMS COMPANY PNEUMATIC ATOMIZING NOZZLE

A nozzle of slightly different design was also constructed and proved more successful than the standard type. A drawing of this nozzle appears in Figure 4. The tip of the liquid nozzle projected $\frac{3}{16}$ in. into the fluidized bed, and the atomizing air issued directly from the nozzle body, which was mounted flush with the wall of the dryer. The inside diameter of the liquid nozzle was 0.040 in. Two sizes of atomizing air annuli were used, 0.10-in. ID by 0.154-in. OD, and 0.10-in. ID by 0.118-in. OD.

FIGURE 4
NEW NOZZLE DESIGN USED IN FLUID-BED DRYER

3. Off-gas Handling

The gases leaving the bed passed through four sintered Monel filters contained in the disengaging section. Both bayonet and cylindrical-shape filters were tested during this study (Micrometallic-Pall Mfg. Co. and Cuno Engineering Corp., respectively) and operated equally well. In both cases, the filters were 18 in. long by about 3 in. in diameter and had an average pore size of 10μ . During the initial exploratory runs, porous carbon filters were used, but some difficulty was experienced in sealing the end fittings and preventing powder leakage, so these were superseded by the sintered metal units.

Solids which accumulated on the surface of the filters were periodically removed during a run by reversing the gas flow through the filter. A jet of 35-psig, preheated (200 to 250 C) air was directed into the filter to dislodge the accumulated cake. Initially, the filters were blown back manually on an average of once every 15 min. Later, an automatic system was installed which provided blowback once every minute. The automatic system consisted of a timer and a solenoid valve which released the pulse of air into a venturi nozzle mounted just downstream of the connection to the filter. The pulse-type blowback avoided continuous accumulation of fines on the filters.

The use of the sintered metal filters was very successful. There was no recurrent tendency for the filters to plug; and even after several hundred hours of operation the pressure drop across a filter remained at a reasonable level (Δp of 10 to 15 in. of water at a flow rate of one scfm air). The filters showed no sign of physical deterioration with respect to corrosion or mechanical deformity.

The off-gas leaving the filters passed through a condenser-scrubber system before entering the main building exhaust. The condenser consisted of a pipe in which a series of water-cooled copper coils was inserted to effect the condensation of water vapor and hydrogen fluoride. This condenser was mounted above a large Monel tank which served as a reservoir for the condensate. In runs which employed the addition of anhydrous hydrogen fluoride to the fluid-bed reactor, the off-gas was processed in a packed-column, recirculating caustic scrubber.

4. Process Materials

In the fluid-bed drying step the uranium-zirconium-fluoride salt solution is sprayed onto a fluidized base of granular material which provides the primary heat transfer surface for evaporating the solvent. The bulk of the salts are deposited as a uniform coating on the bed particles, while a small fraction of the spray droplets dry in the gas phase forming "seed" particles. Since the process is continuous, the starting bed material is gradually withdrawn and the bed eventually consists of the dried salts in a granular form. A discussion of the various materials used in this process follows.

a. Feed Solutions

The zirconium tetrafluoride feed solutions were prepared either from a solution of zirconium tetrafluoride purchased from the General Chemical Division of Allied Chemical Corp., or by redissolving dryer products in hydrofluoric acid. The dissolution of dryer products was effected by mixing a sufficient quantity of solids, water, and hydrofluoric acid (48 percent) in a steam-heated Monel vessel at 80 C for approximately 20 hr. Eighty-liter batches were normally prepared. The final solution contained nominally 1.3 M zirconium, 0.7 M acid, and 0.007 M uranium. For more concentrated zirconium feeds, up to 3.6 M, additional pure zirconium tetrafluoride salt or dryer products were merely dissolved in the dilute solutions. The uranium was added to the feed solutions in the form of uranyl fluoride in amounts equivalent to 1.5 weight percent alloy. In a few instances up to 10 weight percent uranium equivalent was added.

Since the dryer products often contained such insoluble compounds as calcium fluoride and refractory zirconium oxide (used as starting bed materials), a residue usually remained after dissolution.

For this reason, and the inconvenience of the long dissolution time, the commercial solution of zirconium tetrafluoride was more frequently used. This solution consistently analyzed as 1.3 M zirconium and 0.3 M acid. In order to prepare a solution which simulated the dissolution of uranium-Zircaloy-2 alloys, sufficient amounts of stannic chloride pentahydrate, ferric fluoride, chromium trioxide, and nickel chloride hexahydrate were added.

Part of the development work concerned the processing of slurries produced by precipitating the uranium as uranium tetrafluoride in a high-acid medium before the solution was sprayed into the dryer. Laboratory studies developed the technique of reducing the hexavalent uranium in low-acid solutions to tetravalent uranium (normally insoluble in the concentrations employed) with stannous chloride. The reduced solution, though metastable, remained free of precipitate for the length of the test period, which was several weeks. Precipitation was effected upon addition of more hydrofluoric acid (in excess of one molar). In the pilot plant, the precipitation was actually effected in the feed line just upstream of the spray nozzle by pumping a sidestream of aqueous hydrofluoric acid (48 percent) into the main feed stream.

b. Starting Bed Materials

Two materials were used as starting beds, calcium fluoride (native fluorspar, ground to -20, +200 mesh), and a refractory zirconium oxide (bubble-grade) available in the desired size range from the Norton Company. Calcium fluoride, used initially, was believed to be quite suitable since it is completely inert to hydrofluoric acid and fluorine, and possesses a high melting point. However, there was a considerable tendency for this material to cake into large agglomerates during the drying operation. Since a fresh bed of inerts was not used for each run (rather the final bed from one run was used as the starting bed for the subsequent one), these difficulties were only encountered during the preliminary work.

Use of the refractory oxide was generally more satisfactory although this material agglomerated excessively during operation of the dryer with high rates of liquid feed. This problem was overcome by pre-coating the material at a low liquid feed rate (<50 ml/min). The pre-coating technique did not prove successful with the calcium fluoride.

c. Other Reagents

Anhydrous hydrogen fluoride used in the high-temperature hydrofluorination of dryer products was supplied in standard 100-lb cylinders. No effort was made to purify the acid to remove either the water or sulfur content. Laboratory-supplied high- and low-pressure air and nitrogen were used as fluidizing and atomizing gases.

5. General Operating Procedure

The procedure followed in starting the fluid-bed drying runs is detailed herewith, and was essentially identical for both the 3- and 6-in.-diameter columns. Any modifications employed in particular runs will be described in the discussion of that particular case. The quantities mentioned are those for the larger unit. The starting bed was charged to the reactor through an elevated side port located just below the disengaging section of the reactor. While the bed was being charged, all openings (pressure taps, nozzle ports, etc.) into the reactor were purged with air or nitrogen to prevent solids accumulation. Approximately 10 to 16 kg of material (11 to 17 in. of static-bed height) was used per charge. The bed was fluidized with air or nitrogen during the heating period. After the bed temperature was stabilized at the desired value, water was introduced into the reactor through the liquid nozzle at a rate equal to the desired feed rate. The zirconium tetrafluoride feed was introduced to the reactor after final adjustments were made on the heaters to accommodate the additional heat requirements. The fluidizing gas velocity ranged from 0.7 to 2.0 ft/sec at process conditions, and bed temperatures ranged from 240 to 450 C. The range of feed rate studied was from 40 to 210 ml/min. A run was continued for a specified number of hours unless premature termination was necessary due to caking of the bed, or plugging in the spray nozzle. Caking of the bed was usually noticed by a change in the bed weight manometer reading; either the pressure drop across the bed decreased or the fluctuation in the level of the manometer fluid ceased. Bed caking also was detected in some instances by nonuniformity of bed temperature indicating poor fluidization.

The shutdown procedure followed was as follows: (1) flush the feed line with water; (2) shut off all heat to the reactor; (3) purge feed line with air and reduce atomizing air rate; (4) reduce fluidizing gas rate and remove the bed from the column.

B. Fluid-bed Dryer Operations

The work in the fluid-bed dryers is divided into studies on three types of feed solutions: (1) dilute zirconium, about 1.4 M; (2) slurry feeds, dilute zirconium and precipitated uranium tetrafluoride; and (3) concentrated zirconium, up to 3.6 M. Most of the work involved the processing of the dilute feed solutions. These are similar to those now being processed at the Idaho Chemical Processing Plant.⁽⁵⁾ In addition, solutions are referred to as low in acid, about 0.7 M (fluoride to zirconium mole ratio of 4.5), or high in acid, about 9 M (fluoride to zirconium mole ratio of 10). The discussion includes nozzle operation and design, particle size effects, and chemical composition of the dryer product.

1. Dryer Operation Involving Dilute Feeds

a. Preliminary Investigations in the Three-inch Fluid-bed Reactor

Fluid-bed operations on the drying of zirconium tetra-fluoride solutions were commenced in a 3-in.-diameter Monel column. The first bed material was calcium fluoride (fluorspar) ground to minus 40 mesh size. During the course of several continuous runs, the calcium fluoride was gradually displaced by the uranium-zirconium-fluoride products, which were then used as starting materials for the subsequent runs. The work in the 3-in. unit included a preliminary study of the operating variables listed in Table 1.

Table 1

VARIABLES STUDIED IN PRELIMINARY OPERATION OF
A THREE-INCH FLUID-BED DRYER

Variable	Range Studied
Bed Temperature	250 to 350 C
Liquid Nozzle Diameter	0.016 and 0.020 in.
Nozzle Atomizing Pressure	15 and 30 psig
Fluidizing Gas Velocity	0.9 to 2.0 ft/sec
Feed Composition, F/Zr Mole ratio	4.5 and 10.0
Feed Rate	15 to 24 ml/min

An apparent effect of fluidizing velocity on stable column operation was found in a series of three runs made at 300 C using velocities of 1.0, 1.4, and 1.9 ft/sec. In brief, results were as follows:

Fluidizing Speed (ft/sec)	Effect Noted
1.0	Bed caked in 2 hr
1.4	Operation improved, but some agglomerates formed after 6 hr
1.9	Bed free from lumps - duration of run, 10 hr

On the basis of these data, a nominal fluidizing velocity of 2 ft/sec was employed during most of the ensuing experiments.

A series of runs made at bed temperatures ranging from 250 to 350 C indicated that more satisfactory operation would be achieved at the higher temperature. Again, the criterion for the evaluation was the presence of lumps within the final bed. It should be mentioned that the results observed in the 3-in. column were not always substantiated by those obtained in subsequent work in the 6-in. unit. Also, in many instances, definite effects as regards column operation or particle size changes could not be associated with a particular change in a variable, although invaluable experience was gained in the operation of the 3-in. unit. An early objective in the operation of this reactor was to prepare uranium-bearing solids which could be fluorinated to demonstrate the separation and recovery of the uranium values. Equally important was a demonstration of continuous trouble-free operation of a fluid-bed spray dryer.

The major problem areas in these demonstration runs were associated with nozzle operation and control of particle size. Material often collected on the face of the nozzle and tended to disrupt the atomization pattern. In many instances this led to partial or complete caking of the bed. In a few cases, the nozzle plugged internally, and this was attributed to small, undissolved particles in the feed solution. This problem was almost entirely obviated by using larger-sized nozzles. The use of clean-out needles often released internal plugs within the nozzle; however, the needles tended to corrode rapidly and were easily broken.

b. Processing Dilute Feeds in the Six-inch Fluid-bed Reactor

Some of the problems associated with the small-scale dryer were expected to be relieved with scale-up, so operations were shifted to a 6-in.-diameter column and the range of operating variables was expanded. Similar conditions were used for the slurry feeds as well as the dilute and concentrated zirconium feed solutions, so these will be summarized only once.

(1) Operating Variables

The range of operating variables is summarized in Table 2. Bed temperatures ranged from 240 to 450 C and feed rates from 45 to 190 ml/min [equivalent to 15.3 gal/(hr)(sq ft reactor cross section)]. The majority of the work was performed with 0.028-in.- and 0.040-in.-diameter nozzles. In some of the work, nozzles were installed in two of the nozzle ports provided (referred to as dual-nozzle operation, see page 22). The atomizing gas pressure ranged from 15 to 45 psig, with 30 psig (~2.2 scfm) being used most frequently. Fluidizing gas velocities were 0.7 to 2 ft/sec (~12 scfm) at column conditions. Auxiliary attrition jets were employed in many instances to provide small "seed" particles which in turn helped to overcome the particle growth problem.

As much as 5 scfm air was used for attrition. Operating time for a particular set of conditions was accumulated by runs lasting over several days with voluntary shutdowns and startups in between. The longest period of uninterrupted operation was 54 hr.

Table 2

RANGE OF OPERATING VARIABLES IN RUNS EMPLOYING
DILUTE (1.5 M) ZIRCONIUM TETRAFLUORIDE FEED SOLUTIONS

Equipment: 6-in.-diameter reactor

Fluoride-to-Zirconium Mole Ratio in Feed: 4.5 (low acid), and
10 (high acid)

Uranium Concentration in Feed: 0.01 to 0.07 M

Liquid Nozzle Diameter: 0.028 in. and 0.040 in. (Spraying Systems Co.)

Atomizing Gas Pressure: 30 psig (2.2 scfm)

Nozzle Position: 5.5 or 11 in. above gas dispersion plate

Feed Rate: 45 to 190 ml/min

Bed Temperature: 235 to 450 C

Fluidizing Gas Velocity: 0.7 to 2.0 ft/sec at column conditions

Attrition Jet Orifice Diameter: 0.047 in.

Attrition Air Rate: 0.8 to 2.0 scfm

Run Time: 4 to 54 hr (accumulated on successive days with voluntary shutdown each day)

(2) Results and Discussion

The major problems encountered in all of the dryer operations were those associated with the starting bed material, nozzle operation and design, and particle size effects, as discussed below. Various species of zirconium compounds were found in the dryer product, the types and quantity of each depending primarily on dryer temperature, residence time of solids in the dryer, and the acid concentration of the feed solution, (a discussion of these begins on page 33). No other temperature effect was noted in the operation of the 6-in. dryer as opposed to the preliminary results found in the 3-in. column experiments.

(a) Starting Bed Material

Many of the first series of runs were terminated because of caking of the bed. A starting bed of calcium fluoride was used in these cases, and much of the difficulty associated with bed caking was

believed due to the incompatibility of calcium fluoride in the spray drying of zirconium tetrafluoride solutions. Refractory-grade zirconium oxide was then employed as a starting bed material. It was found that successful operation was readily achieved by operating the dryer initially at a low feed rate (~ 50 ml/min) for several hours, thus precoating the oxide particles with a thin layer of zirconium fluoride. The rate could then gradually be increased to the desired operating condition. It was not found possible to precoat calcium fluoride particles satisfactorily in order to preclude the formation of large agglomerates; bed caking occurred within 4 hr in all cases.

Since the starting inert bed materials are gradually displaced by the continuous withdrawal of material as it is produced, these "bed" problems may not be of process significance, especially since the dryer products, themselves, were found to be completely compatible with subsequent dryer operation. Successful operation was also achieved when the residues from dryer product fluorination experiments were used as a starting bed. This material was primarily zirconium tetrafluoride.

(b) Nozzle Operation and Particle Size Effects

The primary evaluation of the fluid-bed dryer runs was based on the uniformity of the particle size distribution throughout the course of a run. Ideally, the particle sizes would remain uniformly distributed between 40 and 200 mesh and particle growth would be limited. Before any analysis of the variable affecting particle growth could be made, however, it was necessary that the spray nozzle function properly. Any distortion of the atomized spray, say from a diffuse pattern to a concentrated jet, would be expected to alter the manner of particle growth grossly.

During many runs a lump of agglomerated particles formed on the face of the nozzle, producing a distorted spray pattern which often contributed directly to the termination of the runs. Actually, several lumps formed during the course of a single run; one agglomerate would break off the nozzle face and another growth would be initiated. As many as a dozen or more such agglomerates were found in the final bed in some cases. Several runs were made to investigate the cause of these growths on the nozzles and arrive at a nozzle design which would avoid the formation of the agglomerates.

Runs Employing Dual-spray Nozzles

Since nozzle agglomerates were often not produced during runs at low feed rates, it was hoped an investigation of the effect of feed flow rate through the nozzle might prove decisive. Nozzles were installed in the reactor at 5.5 and 11 in. above the gas-dispersion plate at an angle of 90 degrees from each other. Separate pumps were provided for each nozzle, and identical flow rates were maintained. Flow rates from 45 to 70 ml/min per nozzle were employed.

Continual particle growth occurred at a rate nearly identical with that observed previously in single-nozzle runs. Also, nozzle agglomerates were found as frequently during this series of tests as in previous runs. For one series of runs, one of the nozzles (Spraying Systems Co.) was redesigned to allow the nozzle face to project $\frac{1}{4}$ in. into the fluidized bed. The design was intended to allow "wiping" of the nozzle face by the motion of the fluidized particles, thus preventing the formation of the nozzle agglomerates. However, no improvement was noted with this projecting nozzle.

Operation with a New Nozzle Design

A new nozzle was designed to avoid the features which seemed to contribute to the formation of solid material on the liquid nozzles used in the previous cases. This nozzle (Figure 4) had no air cap in the proximity of the liquid nozzle and, therefore, provided little surface on which solid material could collect. The liquid nozzle was designed to protrude $\frac{3}{16}$ in. beyond the atomizing air annulus into the fluidized bed. The atomizing air issued directly from the nozzle body which was mounted flush with the wall of the reactor. This design probably prevented the wetted fluidized particles, momentarily in the vicinity of the protruding liquid nozzle, from coming in contact with the nozzle, since the high-velocity atomizing air stream accelerated them from the area.

Two different sizes of atomizing air annuli were tested with the new nozzle: 0.118-in. OD by 0.100-in. ID, and 0.154-in. OD by 0.100-in. ID. The larger annulus required a relatively high air rate (5.5 scfm) for proper functioning of the nozzle.

Table 3 summarizes the runs made with dilute zirconium tetrafluoride feed solutions employing the new nozzle design. Successful operation of the fluid-bed dryer was achieved at temperatures of 240, 300, and 350 C with this new nozzle, and with feed rates to 210 ml/min [17 gal/(hr)(sq ft)]. No growths were observed on the nozzle itself or found in the bed. Total run time accumulated with this nozzle was about 160 hr.

(c) Particle Growth and Particle Size Control

Most of the preliminary runs indicated that particle growth occurred at a rate which might cause the eventual termination of the runs because of excessive fluidizing gas requirements. Means of controlling particle size in the bed by direct attrition jets were evaluated.

Particle Growth

Particle growth as observed in the fluid-bed dryer is depicted graphically in Figure 5, a plot of two of the screen fractions as a function of time for a 34-hr continuous run.

Table 3

SUMMARY OF RUNS EMPLOYING NEW SPRAY NOZZLE DESIGN

Equipment 6-in fluid-bed reactor
 Zirconium Concentration in Feed 1.5 M nominal
 Uranium Concentration in Feed 0.01 M
 Fluoride-to-Zirconium Mole Ratio 10 except 4.5 for ZCP-72
 and ZCP-74
 Liquid Nozzle Diameter (see Figure 4) 0.040 in
 Attrition Air Jet Orifice Diameter 0.047 in
 Internal Autoresistive Heater Power Input 4.0 to 5.7 kva
 (Runs ZCP-72 and ZCP-74 only)

Run Number	Average Feed Rate (ml/min)	Bed Temperature (C)	Attrition Jet Air Rate (scfm)	Total Fluidizing Air Velocity ^a (ft/sec)	Atomizing Air Rate (scfm)	Run Time ^e (hr)
ZCP-67	60	300	0.8	1.2	5.5 ^b	22.3
ZCP-68	60-92	240	0.84 ^d	1.0 ^d	5.5 ^b	36.3
ZCP-69	140	240	-	0.90	5.7 ^b	5.2
ZCP-70	94	300	-	1.1	2.2 ^c	4.0
ZCP-71	72	350	1.8	1.4-1.7	2.2-3.3 ^c	54.5
ZCP-72	65-210	300	1.8	1.4	2.2 ^c	12.0
ZCP-74	155	240	1.8	1.4	5.8-3.3 ^b	24.8

^a Includes attrition jet air. Does not include gas introduced by feed or from atomization

^b Atomizing air annulus OD 0.154 in

^c Atomizing air annulus OD 0.118 in

^d Attrition jet air not used during first 23 hr, total velocity 0.90 ft/sec

^e Run time included several voluntary startups and shutdowns

FIGURE 5

 PARTICLE GROWTH OBSERVED DURING DRYING OF
 1.3 M ZIRCONIUM TETRAFLUORIDE SOLUTION

Bed Temperature: 300 C
 Feed Rate: 80 ml/min
 Atomizing Gas Pressure:
 30 psig (2.2 scfm)
 Liquid Nozzle Diameter:
 0.040 in. (Spraying
 Systems Co.)

The run commenced with a bed containing 13 percent -20 +40 mesh particles, and after 34 hr the bed contained 99.9 percent plus 40 mesh particles. As a result of the continued particle growth, the minimum fluidizing velocity for the bed approached and finally exceeded the velocity maintained at the column inlet (2.0 ft/sec). The minimum gas velocity for adequate fluidization of the final bed was determined to be 2.3 ft/sec. The lack of fluidization which occurred during the final hours of operation surprisingly did not contribute to any immediate operational difficulties. However, the bed was not being adequately fluidized, as indicated by the large temperature gradient measured by thermocouples at two points in the bed about 12 in. apart. By the end of the run the gradient was 15 degrees; the column normally operated with about a three-degree differential.

A complete plot of the screen analysis data is given in Figure 6. These data show that as particles grow they tend to accumulate in a given size range until that fraction becomes saturated, and then proceed to accumulate in the next larger size range. Similar behavior has been observed by Lee.⁽¹³⁾

FIGURE 6
PARTICLE SIZE DISTRIBUTION IN
RUN SHOWING CONTINUOUS
PARTICLE GROWTH

Zirconium Concentration in Feed: 1.3 M
 Feed Rate: 80 ml/min
 Bed Temperature: 300 C
 Atomizing Gas Pressure: 30 psig (2.2 scfm)
 Liquid Nozzle Diameter: 0.040 in. (Spraying Systems Co.)

Attrition Tests

The growth patterns sustained indicated that the fluid-bed dryer could not be operated for extended periods unless some means were provided whereby the particle growth was halted. Consequently, a series of tests was performed in the 3-in.-diameter Monel column to ascertain the amount of attrition produced by the introduction of a high-velocity air jet into a fluidized bed of dryer product. The extent of attrition was determined by calculating the mean volume diameter,* of the bed before and after the test. No liquid feed was used in these tests, and all of the tests were of 6-hr duration. Three types of air jets were evaluated:

- (1) spray nozzles with orifices ranging from 0.016 to 0.060 in.,
- (2) the air annulus of a 0.040-in. spray nozzle with an area equivalent to a circular nozzle opening of 0.066 in., and
- (3) a 0.047-in. orifice drilled in the wall of a horizontal tube.

The horizontal tube was installed such that the air jet was directed vertically upward, concurrent with the fluidizing gas, rather than horizontally toward the opposite wall as in all other tests with spray-nozzle orifices. This was expected to remove any target-grinding effect resulting from particles colliding with the opposite wall. The annulus-type jet was tested to ascertain whether the atomizing air of the spray nozzle could provide a reasonable rate of attrition.

The results summarized in Table 4 and graphically presented in Figure 7 suggest that the rate of attrition expressed as the decrease in the average mean volume particle diameter is a linear function of the mass flow rate of air in the flow range studied. Since in all the tests the velocity of the air from the nozzles or annuli was near the sonic velocity, the energy transferred to the particles was only a function of the mass flow rate of the air. The flow from a sharp-edged orifice, however, apparently does not follow this behavior; the results indicate that the attrition produced by the orifice jet was much greater than that produced by the other types for equivalent air flows. Typical results were 0.046-mm/hr decrease in average particle diameter for the orifice jet and 0.028-mm/hr decrease for a 0.060-in. nozzle. The quantity of air used in the annulus tests was equivalent to the amount used in atomizing the liquid feed in the dryer runs.

*The mean volume diameter is defined by the equation:

$$d_v = \frac{\sqrt[3]{\sum n_i d_i^3}}{N} ,$$

where n_i = number of particles in sieve fraction i
 d_i = diameter of particles in sieve fraction i
 N = total number of particles in sample

Table 4

ATTRITION OF FLUID-BED DRYER PRODUCT PARTICLES BY AN AIR JET

Equipment: 3-in.-diameter reactor

Bed Weight: 2.5 kg

Fluidizing Gas Velocity: 2 ft/sec

Time: 6 hr

Temperature: 28 C (room temperature)

Type of Jet	Orifice Diameter (in.)	Supply Air Pressure (psia)	Air Flow Rate $\times 10^{-4}$ (lb/sec)	Average Rate of Change of Particle Diameter ^a (mm/hr)
Nozzle	0.016	55	2.55	-0.010
Nozzle	0.016	95	4.29	-0.009
Nozzle	0.040	45	12.8	-0.015
Nozzle	0.060	45	28.9	-0.028
Annulus	0.066 ^b	75	33.8	-0.027
Annulus	0.066 ^b	95	38.0	-0.033
Orifice	0.047	75	30.4	-0.046

^a Particle diameter calculated as $d_v = \frac{\sqrt[3]{\sum n_i d_i^3}}{N}$.

^b Diameter of a circle equal in area to the air annulus used with a 0.040-in. pneumatic spray nozzle.

FIGURE 7

ATTRITION OF FLUID-BED DRYER PARTICLES BY AN AIR JET

Actually the power required to atomize 50 ml/min of liquid into 15-micron droplets is very small compared with that available in the high-velocity atomizing air stream (~ 0.02 ft-lb/sec compared to ~ 30 ft-lb/sec). During dryer operation some attrition might be occurring due to the excess energy available, but at a rate too low to be of consequence, because of the relatively low friability of the zirconium fluoride particles produced. In other systems which produce a product of a more friable nature, the excess energy of the atomizing air might be sufficient to control particle size.

Evaluation of Particle Friability

In order to evaluate the problem of particle growth more fully an apparatus was installed to measure the degree of particle friability by an Attrition Index.⁽¹⁴⁾ Various powder samples were tested under standardized conditions and compared in terms of this index.

The apparatus consisted of a 3-ft section of one-in.-ID glass pipe topped by a 3-in.-ID section which contained a porous metal bayonet filter for retaining solids in the test column. The attrition air entered the column through a 0.016-in. hole drilled in the center of a $\frac{1}{16}$ -in.-thick aluminum disc inserted in the bottom of the column. High-pressure air was reduced to 62 psig (considered standard for this test) with a pressure-reducing valve and metered by a needle valve through a rotameter. For target-grinding tests, as opposed to jet-grinding, a small plate was affixed about $\frac{1}{2}$ in. above the orifice to serve as a target.

A 100-g sample of a particular size range (usually 60 to 100 mesh) was charged to the column. An air rate of 0.26 scfm was used. The tests were run for one hour and the material, including filter fines, was removed and screened. The results, shown in Table 5, are reported in terms of an Attrition Index which is expressed as the percent of minus 100 mesh material produced in the "standard" test period. The Attrition Index for zirconium fluoride powders ranged from about 5 to 30, with the material prepared at higher temperatures (350 and 450 C) having lower values than material made at 300 C. The zirconium fluoride prepared from feed having a fluoride-to-zirconium mole ratio of ten, considered as high-acid type (Run ZCP-71), had the lowest rate of attrition of all the materials tested. The target-attrition tests gave index values greater than twice those of the jet-attrition tests. For comparison, tests performed with aluminum oxide prepared from calcined aluminum nitrate solutions⁽⁸⁾ indicated that this material was more subject to attrition than zirconium tetrafluoride powder. During the processing of the aluminum nitrate solutions it was not found necessary to provide excess attrition to control particle growth; evidently, sufficient attrition occurs to provide nuclei for the formation of new particles.

Testing of Attrition Jets in the Fluid-bed Dryer

Several runs were made in the fluid-bed dryer which successfully demonstrated the use of air-jet attrition as a means for controlling particle growth. The initial successful demonstration of the auxiliary attrition technique was made in Runs ZCP-60 and 61. The feed rate for both runs was 100 ml/min and the attrition air rate was 1.8 scfm. During Run ZCP-60, made at 300 C, sufficient attrition was provided to increase the minus 200 mesh fraction from 7 to 27 percent in 12 hr. A corresponding decrease in the plus 60 mesh fraction occurred concurrently (see Figure 8a). The same quantity of attrition air in Run ZCP-61, made at 235 C, however, did not produce an excessive amount of fines as above, but was adequate to inhibit particle growth. Both the minus 200 mesh and plus 60 mesh fractions oscillated within rather wide ranges during the 28-hr run (see Figure 8b).

Even better control of particle size distribution was achieved in Run ZCP-67, made at 240 C, using the new nozzle design (see Figure 8c). The large air annulus of the new nozzle required a much larger amount of atomizing air than that used in previous runs, and apparently effected some attrition requiring only a small amount of auxiliary attrition jet air (0.8 scfm) to control particle growth. A comparison of Run ZCP-67 with ZCP-61 indicates that slightly better control of particle size distribution was achieved by operating the dryer at a reduced feed rate.

The variation in attrition results may very well have been due to the friability of the material produced. From the data in Table 5, the product from Run ZCP-60, where excessive fines were produced, had an Attrition Index of 30, the highest of all dryer product powders measured. The friability may also be related to the composition of the powder (or, in essence, the dryer conditions), since 300 C material contains a large fraction of zirconyl fluoride, while the product from the 240 C run (ZCP-61) was primarily zirconium tetrafluoride.

Two runs of extended duration were made which permitted some insight into the effects of some of the variables on particle growth. During Runs ZCP-68, 69 and 71, the effects of feed rate, auxiliary attrition jet air rate, and fluidizing gas rate were observed. The changes in particle size distribution for these runs are presented in Figures 9a and 9b.

During the first 14 hr of Runs ZCP-68-69, a high rate of fines production occurred, probably due to the large quantity of atomizing air employed (5.5 scfm). The production of fines was curtailed by increasing the feed rate from 60 to 92 ml/min. The seemingly abrupt change in fines concentration with a corresponding increase in the plus 60 mesh fraction accompanying this feed rate change is not readily explained, since a more gradual change before reaching the steady-state condition would be expected. An increase in total air flow due to the introduction of

jet attrition air after 23 hr lowered the steady-state value of the minus 200 mesh fraction from 26 to 17 percent. This may have been due to a ten percent increase in air throughput which elutriated some fines from the bed, although a similar effect was not noticed in Run ZCP-71 when the fluidizing air rate was increased 20 percent.

Bed Temperature: 300 C
Nozzle Diameter: 0.040 in.
Feed Rate: 100 ml/min
Attrition Air Rate: 1.8 scfm
Attrition Jet Orifice
Diameter: 0.047 in.

Run ZCP-60

(a)

Bed Temperature: 235 C
Nozzle Diameter: 0.040 in.
Feed Rate: 100 ml/min
Attrition Air Rate: 1.8 scfm
Attrition Jet Orifice
Diameter: 0.047 in.

Run ZCP-61

(b)

Bed Temperature: 240 C
Nozzle Diameter: 0.040 in.
Feed Rate: 60 ml/min
Attrition Air Rate: 0.8 scfm
Attrition Jet Orifice
Diameter: 0.047 in.

Run ZCP-70

(c)

FIGURE 8 (a) (b) (c)
EFFECT OF JET ATTRITION
ON PARTICLE SIZE DISTRIBUTION
DURING FLUID-BED
DRYER RUNS

Table 5

CONDITIONS AND RESULTS OF ATTRITION TESTS

Duration of Test: 1 hr
 Sample Weight: 100 g
 Attrition Orifice Size: 0.016 in.
 Attrition Air Rate: 0.26 scfm

Test Materials

A. Zirconium fluoride particles from fluid-bed dryer run

B. Product from fluid-bed calcination of synthetic aluminum
 nitrate waste

Material	Mesh Size	Attrition Index ^a
A. Run ZCP-48 (450 C, F/Zr: 4.5)	20 thru 325	8.4, 12.4, 10.5
	20 thru 325	15.6 ^b , 16.0 ^b , 15.8 ^b
	60 to 100	14.0, 12.6, 14.4, 14.6, 13.1
A. Run ZCP-60 (300 C, F/Zr: 4.5)	60 to 100	32.8, 29.8
	60 to 100	79.5 ^c , 79.5 ^c , 76.9 ^c
A. Run ZCP-71 (350 C, F/Zr: 10)	60 to 100	6.4, 4.2, 6.2
B. Run HWC-117	60 to 100	24.6, 23.6, 23.6

^aNumbers denote results of replicate tests.

^bThese tests were 2 hr long.

^cTarget grinding used.

Bed Temp: 240 C; Feed F/Zr Mole Ratio = 10
 Atomizing Air Annulus Dimensions: 0.154 in. OD, 0.100 in. ID
 Fluidizing Gas Rate: 8.3 scfm (1.1 ft/sec)
 Liquid Nozzle Diameter: 0.040 in.

FIGURE 9 (a) (b)
 PARTICLE SIZE DISTRIBUTION
 DURING EXTENDED FLUID-BED
 DRYER OPERATION

Feed Rate 72 ml/min
 Bed Temperature 350 C
 Attrition Jet Air Rate 1.8 scfm
 Atomizing Air Annulus Dimensions:
 0.118 in. OD, 0.100 in. ID
 F/Zr Mole Ratio in Feed-10
 Atomizing Air Rate 2.2 scfm 0-24 hr
 3.3 scfm 24-54.5 hr

The sharp increase in fines concentration noted at the start of Run ZCP-69 (made as a continuation of Run ZCP-68) was due to excessive attrition caused by the use of full atomizing air flow from the spray-nozzle annulus (5.5 scfm) during startup. The concentration of fines rapidly decreased during the 5-hr run.

Run ZCP-71 was made with a nozzle with a small air annulus, and the amount of attrition resulting from the atomizing air was correspondingly decreased. Since particle growth occurred during the first part of the run, the atomizing air rate was raised from 2.2 to 3.3 scfm to effect more particle attrition. Auxiliary air-jet attrition was supplied by 1.8 scfm of air from a 0.047-in.-diameter orifice. A considerable time lag was noted before the increased attrition from the atomizing air affected the average particle size.

Because of the particle growth which occurred in the middle of the run, it was necessary to increase the fluidizing gas velocity from 1.4 to 1.7 ft/sec to insure that the bed was adequately fluidized. In contrast with Runs ZCP-68-69, neither this increase nor the increase in atomizing air rate had any noticeable effect on the concentration of fine particles in the bed, probably because the concentration of fines at the time these changes were made was very small - less than ten percent below 100 mesh.

The effect of feed flow rate on the amount of auxiliary attrition required to halt particle growth was observed in a later run. At a feed rate of 155 ml/min, it was observed that the previous quantity of air-jet attrition (0.047-in.-diameter orifice; 1.8 scfm air) was not very effective in controlling the particle size distribution. The plus 40 mesh fraction increased from 20 to 42 percent during the 25-hr run, while the minus 60 mesh fraction decreased from 31 to 1.5 percent. Some of the larger particles were formed by agglomeration of smaller ones, in contrast to growth only by coating. Evidently, operation of the fluid-bed dryer at high feed rates requires much more attrition than supplied by the orifice.

A jet-target grinder which had been shown to produce much more attrition than an attrition air jet was installed for Run ZCP-76. A concentrated feed solution was used. The two previous runs made with concentrated feed solutions (ZCP-73 and ZCP-75) indicated that continuous rapid particle growth occurs at moderate feed rates (125 ml/min). The target-grinder consisted of a 0.60-in.-diameter target plate mounted one inch from a 0.040-in.-diameter Spraying Systems Co. nozzle. Air was fed at 90 psig (5.0 scfm) through the liquid orifice of this auxiliary nozzle.

The particle size distribution throughout Run ZCP-76 behaved similarly to that shown in Figure 8c, with reasonably narrow oscillations for the plus 40 mesh and minus 60 mesh fractions.

The starting bed was screened so that it contained only one percent minus 100 mesh particles. At the end of the run of approximately 18 hr, this fraction increased to seven percent and the plus 40 mesh fraction remained the same as in the starting bed. These data indicate satisfactory particle size control can be exercised if sufficient attrition is provided.

(d) Dryer Operation at High Feed Rates

The capacity of the dryer was determined by two factors: first, the rate of heat input into the reactor, and, second, the rate of particle growth at high feed rates. With only the external heaters in use, the capacity of the reactor was limited to approximately 150 ml/min. In order to provide greater throughputs in the 6-in. dryer, an autoresistive heater was installed. This internal Inconel strip heater allowed operation of the dryer at feed rates above 200 ml/min. Only about one-half of the total power required at the higher rates was supplied by the external calrod heaters. It was estimated that the heat-input efficiency of the calrod heaters alone was about 75 percent; the efficiency of the combined external and internal heaters was estimated to be 90 percent. The power level of the internal autoresistive heater was maintained at 4.0 kva except for a short period at 5.7 kva (22 v and 265 amp) during which the feed rate exceeded 190 ml/min. Operation of the dryer at feed rates over 150 ml/min resulted in particle growth in the form of agglomerates as well as by particle coating.

2. Dryer Operations Involving Uranium Tetrafluoride Slurry Feeds

Early work on the fluorination of zirconium fluoride dryer products was not successful, as measured by the extent of uranium removal. It was thought that uranium may be more readily removed during fluorination if the uranium were present in the dryer product as discrete particles rather than homogeneously mixed in the solids. Studies involving the preparation of material in the fluid-bed dryer containing the uranium as precipitated uranium tetrafluoride were therefore made and are discussed below.

a. Preparation of Slurry Feeds

Laboratory studies showed that tetravalent uranium in the form of uranium tetrafluoride was readily precipitated from a zirconium-uranium feed solution by increasing the fluoride-to-zirconium mole ratio from 4.5 to 10 by the addition of hydrofluoric acid. The precipitate initially formed as a colloid which gradually transformed to a crystalline state. When the transformation had progressed sufficiently, discrete particles began to settle from the solution. The transformation from the colloidal to the crystalline state usually commenced in about one to three minutes in dilute (0.007 M) uranium solutions. In more concentrated uranium solutions (0.02 M), the transformation was extremely rapid; particles began to settle from solution immediately after hydrofluoric acid was added.

Since the pilot-plant feed solutions contained hexavalent uranium (added as uranyl fluoride), it was necessary first to add a reducing agent to reduce the uranium to the tetravalent state before the precipitation could be effected. Tests showed that with chromous sulfate or stannous chloride as reducing agents the reduction of uranium was complete in less than one hour at room temperature. At this point the solutions contained a fluoride-to-zirconium mole ratio of 4.5, and even though the solubility of uranium tetrafluoride was exceeded no precipitation occurred. These quasi-stable solutions containing uranium concentrations as high as 0.03 M remained free of precipitate even after standing for periods up to several months. Precipitation could be immediately effected, however, upon addition of more hydrofluoric acid to the solution.

b. Runs Employing Slurry Feed

In the pilot plant, stannous chloride was used as a reducing agent for the uranium. In actual dryer operation, precipitation of uranium tetrafluoride from the zirconium tetrafluoride feed solutions was effected by introducing a side stream of either 49 percent aqueous hydrofluoric acid or anhydrous hydrogen fluoride into the main feed stream upstream from the spray nozzle. The quantity of acid added in the side stream depended on the feed flow rate, and was sufficient to raise the fluoride-to-zirconium mole ratio from 4.5 to 10. A 20-ft coil of plastic tubing was installed in the feed line subsequent to the junction of the hydrogen fluoride side stream. This coil provided a residence time of 4 min at a flow rate of 90 ml/min to allow the uranium tetrafluoride precipitate to form. It was observed through the transparent plastic tubing that the precipitate formed rapidly and was transported by the main stream into the dryer. Fewer runs were made with anhydrous hydrogen fluoride than with aqueous hydrofluoric acid because the flow rate of the anhydrous gas was very sensitive to any pressure buildup downstream from the side stream junction and at times was actually interrupted. Also, there was a tendency for the hydrogen fluoride gas to enter the feed line in slugs which at times completely displaced the liquid in the feed line.

A summary of the runs made using the side stream of aqueous hydrogen fluoride is presented in Table 6. The feed solutions contained about 1.5 M zirconium with uranium concentrations of 0.008 M and 0.02 M, equivalent to 1.5 and 3.5 weight percent uranium alloys. The fluoride-to-zirconium mole ratio in the feed was 4.5. Feed rates ranged from 34 to 112 ml/min.

The first series of runs was made with a Spraying Systems Company nozzle with a liquid nozzle orifice 0.028 in. in diameter; a cleanout needle assembly was employed with the nozzle. Since this nozzle frequently plugged with precipitated uranium tetrafluoride, a larger nozzle, of 0.040-in. diameter, was employed. The larger nozzle relieved most of the plugging

difficulty, and further improvement was achieved by increasing the feed flow rate, thereby creating higher liquid velocities through the nozzle and reducing the residence time for the agglomeration of the uranium tetrafluoride precipitate. In the runs made with 3.5 weight percent uranium, some nozzle plugging occurred at the lower feed rate, 70 ml/min, possibly due to the increased volume of the uranium tetrafluoride precipitate. This difficulty was overcome by adding an air stream to the liquid feed, increasing further the velocity through the nozzle. No plugging of the nozzle occurred at high feed rates when the air purge was used. A total of 72 hr of running time was accumulated in this phase of the work.

Table 6

SUMMARY OF RUNS EMPLOYING URANIUM TETRAFLUORIDE PRECIPITATION

Bed Temperature: 300 C, except 450 C for Run ZCP-39
 Fluidizing Air Velocity: 2 ft/sec at reactor conditions
 Feed Composition, Nominal: 1.5 M zirconium, 6.75 M fluoride

Run Number	Uranium Concentration in Feed (M)	Feed Rate (ml/min)	Sidestream Rate-49% HF (ml/min)	Liquid Nozzle Diameter (in.)	Nozzle Atomizing Pressure (psig)	Total Run Time (hr)
ZCP-22 to 26	0.008	34	12	0.028	45	24.0
ZCP-29	0.008	52	16	0.040	30	7.0
ZCP-30 to 31	0.008	76	23	0.040	30	10.8
ZCP-32	0.008	112	32	0.040	30	4.3
ZCP-39	0.008	90	30	0.040	30	10.6
ZCP-35 to 37	0.02	70	24	0.040	30	11.4
ZCP-38	0.02	100	32	0.040	30	4.0

Studies involving the calcining of slurry feeds were merely exploratory, and this phase of the work was concluded since there were inherent in the scheme potential problems with line and nozzle plugging. Of more serious consequence was the fact that the fluorination of slurry products showed no better uranium removal than other materials where the uranium is completely distributed throughout the solids (see page 55).

3. Use of Concentrated Zirconium Fluoride Feed Solutions

Since the rate of processing nuclear fuel solutions in the drying step of the ADF process is dependent in part on the concentration of the metal salt solution that can be prepared, it would be desirable to process more concentrated feeds. According to Tananayev et al.,⁽⁹⁾ zirconium exhibits a maximum solubility in aqueous hydrogen fluoride at a composition corresponding to 30 percent zirconium oxide, 30 percent hydrogen fluoride, and 40 percent water. This solution contains over twice the concentration of zirconium as the feed now being used. Several experiments were performed to prepare concentrated solutions and to evaluate their utility as dryer feed.

a. Laboratory-scale Dissolutions

A dissolution of zirconium metal turnings was made by slowly adding 250 g of 48 percent hydrofluoric acid to 88.8 g of metal in 71.2 g of water. After the acid was added, the mixture was heated at 65 C for 12 hr under continuous reflux and then cooled to room temperature. No undissolved metal or precipitated zirconium fluoride salt was evident. The solution had a density of 1.59 g/cc and chemical analyses (see Table 7) showed a zirconium molarity of 3.6. The solution remained essentially stable except for trace amounts of a very fine precipitate which formed over a 65-day period.

Table 7

CHEMICAL ANALYSES OF CONCENTRATED ZIRCONIUM
FLUORIDE SOLUTIONS

Analysis	Zirconium Metal Dissolution	Zirconium Tetrafluoride Dissolution
Zirconium	3.6 <u>M</u>	3.8 <u>M</u>
Total Fluoride	23.3 <u>M</u>	24.8 <u>M</u>
Acidity	8.27 <u>N</u>	9.28 <u>N</u>
Density	1.59 g/cc	1.63 g/cc

Since synthetic feed solutions prepared by dissolution of zirconium fluoride were used in the ADF process development work, another concentrated solution was prepared by dissolving 326 g of zirconium tetrafluoride in 192 g of 48 percent hydrofluoric acid and 283 g of water. The major fraction of salt dissolved in the first 12 hr, however, after 40 hr of heating under reflux at 65 C, about 5 to 10 percent of the material remained undissolved. The filtered solution had a density of 1.63 g/cc and a zirconium concentration of 3.8 M (see Table 7). This solution also remained stable. The experiment was repeated to determine if zirconium tetrafluoride could be dissolved without leaving an insoluble residue. The quantities of ingredients were adjusted so that less zirconium tetrafluoride and more water were used. However, an insoluble residue still remained after the materials were heated and mixed for 40 hr. Overall results appeared promising, so a few experiments were conducted on a pilot scale.

b. Pilot-scale Processing of Concentrated Feeds

(1) Feed Preparation and Operating Conditions

Concentrated feed solutions were made by dissolving previously prepared fluid-bed dryer products in aqueous hydrofluoric acid. The final solutions ranged in zirconium concentration from 2.3 to 3.6 M and contained about 10 M free acid, giving a fluoride to zirconium mole ratio of about seven. The solutions remained stable as in the laboratory tests.

The runs made with these feed solutions are detailed in Table 8. Dryer temperatures ranged from 300 to 385 C. The attrition air jet was employed in these runs to curtail particle growth. In Run ZCP-76 a jet target-grinder was substituted for the ordinary attrition jet. The device consisted of a 0.60-in.-diameter target plate affixed one inch in front of a Spraying Systems Co. spray nozzle and was mounted in the same position as the liquid feed spray nozzle but displaced 90° on the periphery of the column. Approximately 5 scfm of air was supplied through the 0.040-in. liquid side of the nozzle to provide the desired attrition.

Table 8

OPERATING CONDITIONS FOR RUNS EMPLOYING CONCENTRATED
ZIRCONIUM TETRAFLUORIDE FEED SOLUTIONS

Equipment: 6-in.-diameter Inconel Reactor
Fluoride to Zirconium Mole Ratio in Feed: 7.0
Atomizing Gas Rate: 3.3 scfm
Liquid Nozzle Diameter: 0.040 in.
Attrition Air Jet Orifice Diameter: 0.047 in. (Runs ZCP-73 and 75 only)
Target Jet Grinder Orifice Diameter: 0.040 in. (Run ZCP-76 only)
Internal Autoresistive Heater Power Input: 4.2 kva
Anhydrous Hydrogen Fluoride Rate: Four moles per mole zirconium in the feed
(Runs ZCP-75 and 76 only)
Fluidizing Gas Velocity: 1.4 ft/sec (includes HF when used)

Run Number	Zirconium Concentration in Feed (M)	Feed Rate (ml/min)	Bed Temperature (C)	Atomizing Air Annulus Diameter ^a (in.)	Attrition Jet Air Rate (scfm)	Total Run Time (hr)
ZCP-73	3.6	60-160	300	0.118	1.8	8.5
ZCP-75	2.3	125	355	0.154	1.8	11.8
ZCP-76	2.8	90-60	385	0.118	5.0	18.2

^a Annulus inside diameter for both nozzles was 0.100 in.

The atomizing nozzles used in these tests were the same as those which were successfully employed in processing dilute feed solutions. Feed rates for the concentrated solutions were up to 160 ml/min, which represented an increase in throughput by a factor of 2.7, compared to 160 ml/min of dilute feed. During Runs ZCP-75 and 76, anhydrous hydrogen fluoride was introduced with the fluidizing gas at a rate to provide four moles of hydrogen fluoride per mole of zirconium in the feed. This addition of hydrogen fluoride was an effort to produce a product which would contain a minimum amount of oxygen, considered desirable for the subsequent fluorination step.

(2) Results of Runs with Concentrated Feeds

Particle growth in the form of agglomerates as well as by surface coating occurred in the runs where only the jet attrition was used. The jet target-grinder, however, was successful in maintaining a fairly uniform particle size distribution (in Run ZCP-76). In this case, the plus 40 mesh fraction oscillated between 50 and 60 percent and the bed contained less than five percent plus 20 mesh particles. In contrast, the plus 40 mesh fraction increased from 25 to 81 percent when only jet attrition was used. Nozzle operation continued to be satisfactory, and no other problems related to handling concentrated feed solutions were evident.

Chemical analyses of the products from these runs indicated that there is no significant difference in the species formed from concentrated feeds compared to those formed by drying dilute solutions.

4. Chemical Composition of Dryer Products

Chemical and X-ray analyses of the products obtained by fluid-bed drying of zirconium tetrafluoride solutions indicated that several different compounds may be produced, depending on the drying conditions. The variables which influenced the formation of these various species were drying temperature, hydrogen fluoride concentration in the reactor, and the residence time of the solids in the reactor. Since there is an appreciable residence time in the reactor, of the order of 8 hr, the solids which form initially continue to react with the environmental gases, water vapor and hydrogen fluoride, tending to approach an equilibrium condition.

During preliminary work it was not possible to predict which zirconium species would be formed in the fluid-bed dryer, since no reference to previous work was found in the literature on the system zirconium tetrafluoride-water vapor-hydrogen fluoride. Of special interest was the effect of temperature on the equilibrium partial pressure of hydrogen fluoride and even more fundamental the reaction of zirconium tetrafluoride and water vapor alone.

The physical properties of some zirconium fluorides have been observed. Haendler⁽¹⁰⁾ found that zirconium tetrafluoride monohydrate evolves both water and hydrogen fluoride upon heating; but the conditions under which the heating was conducted were not described. Tananayev *et al.*,⁽⁹⁾ state that the monohydrate splits off two moles of hydrogen fluoride when heated, one mole at 267 C, the other at 306 C. The final product was zirconyl fluoride (ZrOF_2). Zirconyl fluoride dihydrate decomposes at 400 C through the loss of two moles of hydrogen fluoride and one mole of water to give zirconium oxide.

a. Identification of Fluid-bed Dryer Products

X-ray diffraction analyses of various dryer products indicated that at least four different compounds may be formed in the dryer: zirconium oxide, zirconyl fluoride, and both anhydrous and monohydrated zirconium tetrafluoride (see Table 9). In a few instances, unidentified major phases were present. The α and β polymorphs of zirconium tetrafluoride, as designated in Table 9, refer to the classification of Chretien and Gaudreau.⁽¹¹⁾ Beta zirconium tetrafluoride is the usual form of the compound and is well characterized; the alpha polymorph has been defined only recently.

Table 9

IDENTIFICATION OF DRYER PRODUCTS BY X-RAY DIFFRACTION

Run Number	Fluoride to Zirconium Mole Ratio in Feed (F/Zr)	Dryer Temperature (C)	Chemical Species Identified (major phase)
ZCP-60	4.5	300	ZrOF_2 , βZrF_4 , $\text{ZrF}_4 \cdot \text{H}_2\text{O}$
ZCP-60 HF	Anhydrous HF	435	βZrF_4 , ZrOF_2
ZCP-66	4.5	240	ZrF_4 , $\text{ZrF}_4 \cdot \text{H}_2\text{O}$
ZCP-66 HF	Anhydrous HF	435	βZrF_4
ZCP-73 ^a	7	300	αZrF_4 , $\text{ZrF}_4 \cdot \text{H}_2\text{O}$
ZCP-76 ^a	7 ^b	385	βZrF_4 , unidentified phase
ZCP-31 ^c	10	300	αZrF_4
ZCP-38 ^c	10	300	αZrF_4 , βZrF_4
ZCP-39 ^c	10	450	ZrOF_2 , ZrO_2

^a Feed was concentrated solution of zirconium tetrafluoride.

^b Anhydrous hydrogen fluoride added to fluidizing gas - 4 moles HF per mole Zr in feed.

^c Sidestream of aqueous hydrofluoric acid added to raise F/Zr ratio to ten to precipitate uranium tetrafluoride.

The chemical analyses of representative dryer products are presented in Table 10. Comparison of these data with the information appearing in Table 9 confirms the results obtained by X-ray diffraction. The zirconium concentrations reported for most samples have a low bias, and should be interpreted accordingly.

Table 10

CHEMICAL ANALYSES OF FLUID-BED DRYER PRODUCTS

Run Number	Mole Ratio F/Zr in Feed	Temperature (C)	Constituent (w/o)			
			Zr	F	U	O ^a
ZCP-66	4.5	240	47	40.6	0.64	4.0
ZCP-74	4.5	240	50	41.2	1.07	3.6
ZCP-50	4.5	300	51	32.6	2.48	-
ZCP-60	4.5	300	55	30.9	0.94	6.5
ZCP-72	4.5	300	46	38.6	0.88	-
ZCP-48	4.5	450	67	2.3	0.73	-
ZCP-73	7	300	51	42.4	0.96	2.0
ZCP-75 ^{b,c}	7	355	46	43	-	-
ZCP-76 ^{b,c}	7	385	49	41.3	-	-
ZCP-76 ^d	7	480	50	40.6	-	-
ZCP-31	10	300	47	42.6	0.68	-
ZCP-38	10	300	47	41.8	2.16	3.5
ZCP-71	10	350	48	32.4	-	-
ZCP-39	10	450	56	19.4	0.78	14.8

^aOxygen analyses performed at ORNL by J. C. White.

^bConcentrated zirconium feed solution used.

^cAnhydrous hydrogen fluoride added to fluidizing gas.

^dA 4-hr heat treatment at 480 C of material from Run ZCP-76.

According to these results, several conclusions may be made regarding the types of compounds which will be formed under specific conditions (see Table 11). Both anhydrous and monohydrated zirconium tetrafluoride are the major species formed at 240 C. The nature of the species formed at this temperature is not influenced by the hydrogen fluoride concentration in the feed, whereas at 300 C the effect of the hydrogen fluoride concentration becomes important. Zirconyl fluoride is a major species produced along with both anhydrous and monohydrated zirconium tetrafluoride with feeds containing a fluoride-to-zirconium mole ratio

of 4.5. Only zirconium tetrafluoride, hydrated and anhydrous, is formed at the higher hydrogen fluoride concentrations. The presence of zirconium tetrafluoride monohydrate in the dryer products at 300 C is not incontrovertible, since at temperatures slightly above 300 C the compound decomposes. At 450 C, zirconium oxide is formed from both the high- and low-acid-concentration feeds. Zirconyl fluoride is also formed at 450 C but only with fluoride-to-zirconium mole ratio in the feed of ten (high acid).

Table 11

TYPES OF ZIRCONIUM COMPOUNDS PRODUCED IN
THE FLUID-BED DRYER

Temperature (C)	Fluoride to Zirconium Mole Ratio in Feed	Species Produced
240	4.5	$\text{ZrF}_4 + \text{ZrF}_4 \cdot \text{H}_2\text{O}$
240	10	$\text{ZrF}_4 + \text{ZrF}_4 \cdot \text{H}_2\text{O}$
300	4.5	$\text{ZrOF}_2 + \text{ZrF}_4 + \text{ZrF}_4 \cdot \text{H}_2\text{O}^a$
300	10	$\text{ZrF}_4 + \text{ZrF}_4 \cdot \text{H}_2\text{O}^a$
450	4.5	ZrO_2
450	10	$\text{ZrO}_2 + \text{ZrOF}_2$

^aAt temperatures slightly above 300 C, zirconium tetrafluoride monohydrate decomposes;⁽⁹⁾ therefore, it may not be found in dryer products made above this temperature (see Run ZCP-31 in Table 9).

b. Analysis of Spray-dried Products

Since residence time plays an important role in determining the final product composition, a series of experiments was conducted in which the contact time was very short. These tests were expected to give information regarding the degree of reaction occurring between the solids and the environmental gases. The procedure was to spray zirconium fluoride solutions on the heated wall of the reactor for 10 to 15 min. No fluid bed was used in these tests. The results, which are presented in Table 12, indicate that there is a difference between the spray-dried solids and fluid-bed material produced under similar conditions of temperature and feed. For instance, zirconium tetrafluoride is a constituent of 450 C spray-dried material and is not found in any dryer products made at this temperature. Also, zirconium oxide, a major fraction of dryer product

made at 450 C, was not found in the spray-dried material. Apparently, the short residence time of the spray-dried solids (~15 min) did not allow the zirconium tetrafluoride to undergo pyrohydrolysis to zirconium oxide as was the case in the fluid-bed dryer.

Table 12

RESULTS FROM X-RAY DIFFRACTION ANALYSES OF SPRAY-DRIED^a
ZIRCONIUM TETRAFLUORIDE SOLUTIONS

Sample	Fluoride to Zirconium Mole Ratio in Feed (F/Zr)	Drying Temperature (C)	Species Identified
1	4.5	300	βZrF_4 , $\text{ZrF}_4 \cdot \text{H}_2\text{O}$
2	10	300	Amorphous
3	4.5	450	βZrF_4 , ZrOF_2 , Unidentified Phase
4	10	450	βZrF_4 , ZrOF_2 , Unidentified Phase

^aMaterial prepared by spraying feed solutions on hot surface for 10 to 15 min.

c. Pyrohydrolysis of Zirconium Tetrafluoride

The pyrohydrolysis of zirconium tetrafluoride was studied in a fluid bed to confirm the fact that zirconyl fluoride is a reaction product. The test was made by contacting zirconium tetrafluoride powder with water vapor and hydrogen fluoride in a fluidized bed at concentrations corresponding to a 1 M solution of hydrofluoric acid. Samples of the bed were taken at various intervals and analyzed for fluoride concentrations. The results are plotted in Figure 10. The final bed contained 22 percent fluoride, and X-ray analysis indicated the material was primarily zirconyl fluoride (fluoride concentration in ZrOF_2 is 26.2 percent). From the results obtained from fluoride analyses of intermediate samples, it appears that the pyrohydrolysis proceeds uniformly, and that the reaction proceeds even after a composition corresponding to zirconyl fluoride is reached. Although an intermediate is produced, the pyrohydrolysis proceeds toward the formation of zirconium oxide.

FIGURE 10
REACTION OF ZIRCONIUM TETRAFLUORIDE WITH
AN AIR-HYDROGEN FLUORIDE-STEAM MIXTURE

Equipment: 1-1/2-in.-diameter Monel
Fluid-bed Column
Air Rate: 0.26 scfm
Liquid Rate: 5.5 ml/min
Temperature: 300 C
Hydrogen Fluoride Concentration: 1 M

A reasonable mechanism for the formation of the various species involves the reaction of zirconium tetrafluoride with water vapor to produce zirconyl fluoride and hydrogen fluoride. At high temperature (near 450 C) the pyrohydrolysis produces a considerable quantity of zirconium oxide. The degree of reaction depends on the temperature and the hydrogen fluoride concentration. Thus at 300 C, with a low hydrogen fluoride concentration in the reactor, a considerable quantity of zirconyl fluoride is produced, while with higher hydrogen fluoride concentrations the reaction is suppressed. The hydrogen fluoride concentration also influences the 450 C production of zirconyl fluoride and zirconium oxide. At high hydrogen fluoride concentrations less zirconium oxide is produced in a given time.

d. Hydrofluorination of Dryer Products

During the course of the development work, it was apparent that reaction of fluorine with oxygen-containing dryer products would consume considerable quantities of fluorine, thereby increasing reagent cost. Therefore, the possibility of removing oxygen by a high-temperature reaction with comparatively inexpensive anhydrous hydrogen fluoride was investigated. The oxygen appeared in the dryer product either as a hydrate or in zirconyl fluoride and was expected to be readily removed.

The hydrofluorination runs were made in both the 3-in.-diameter and 6-in.-diameter reactors. The fluidizing gas composition ranged from 27 to 100 percent hydrogen fluoride. The diluent gas was either air or nitrogen. Fluidizing gas velocity was 0.7 ft/sec at column conditions. A summary of the operating conditions appears in Table 13.

Table 13

SUMMARY OF OPERATING CONDITIONS FOR
HYDROFLUORINATION RUNS

Equipment: 6-in.-diameter Inconel Reactor
3-in.-diameter Monel Reactor
(ZCP-60 HF and ZCP-66 HF only)

Fluidizing Gas: Nitrogen or air and hydrogen fluoride

Fluidizing Velocity: 0.7 ft/sec at column conditions

Run Number	Temperature (C)	Time (hr)	Hydrogen Fluoride Concentration (v/o)
ZCP-60 HF	435	5	100
ZCP-66 HF	435	5	100
ZCP-71 HF	450	5.5	50
ZCP-73 HF	460	4.4	50
ZCP-74 HF-A	450	3.7	35 ^a
ZCP-74 HF-B	450	2.5	35 ^a
ZCP-76 HF	460	4.0	35 ^a
ZCP-76 HT ^b	480	3.0	-
ZCP-76 HT-HF	470	3.0	27 ^a

^aHydrogen fluoride diluted with air instead of nitrogen.

^bBed from ZCP-76 heated in air only for 3 hr; no hydrogen fluoride used.

Although the run time was varied from 2.5 to 5.5 hr, there seemed to be no effect of time of these intervals on the residual oxygen content. Oxygen analyses (see Table 14) indicated that most of the oxygen was removed in 2.5 hr. However, it was not possible to remove all the oxygen from the dryer products; the lowest value obtained was 0.76 percent oxygen. Some additional oxygen was removed during fluorination of this material at 700 C; for example, one residue contained 0.31 percent oxygen.

Table 14

EFFECT OF HYDROGEN FLUORIDE REACTION WITH
FLUID-BED DRYER PRODUCT

Mole Ratio F/Zr in Feed	Dryer Temperature (C)	Analysis (w/o)			
		As Produced		After HF Treatment	
		F	O	F	O
4.5	240	40.6	4.0	43.4	1.0
5	240	41.2	3.6	-	1.2 ^a
4.5	300	30.9	6.5	41.3	1.7
7 ^b	300	42.4	2.0	44	0.8
10	350	32.4	-	44.4	-
7 ^b	385	41.3	-	43.6	-

^aResult from 2.5-hr treatment; oxygen content 1.13% after 4-hr run on same material.

^bConcentrated feed used in this case.

X-ray diffraction analyses indicated that the water associated with monohydrated zirconium tetrafluoride was readily removed by hydrofluorination, but that zirconyl fluoride was not very reactive (compare Run ZCP-60 HF with ZCP-66 HF in Table 9). It has been reported⁽¹²⁾ that the hydrofluorination of zirconyl fluoride or zirconium oxide is not readily carried to completion. The optimum temperature of both reactions was found to be 600 C. It was not possible to conduct practical hydrofluorinations at this temperature since zirconium tetrafluoride particles begin to sinter into agglomerates at 550 C. Since the conversion of zirconyl fluoride to zirconium tetrafluoride proceeds slowly, it is not surprising that some residual oxygen appeared in the various hydrofluorination products.

III. FLUORINATION STUDIES FOR RECOVERY OF URANIUM

Each of the types of solids prepared in the fluid-bed dryer were fluorinated in fluid-bed and static-bed reactors with elemental fluorine. The equipment and results are summarized below.

A. Equipment and Procedure

1. Pilot-plant Equipment

The pilot-plant equipment consisted of several fluorination reactors and auxiliary equipment, such as the fluorine supply and off-gas cleanup systems, as discussed below. A schematic layout of the equipment is shown in Figure 11.

a. Fluorination Reactors

Three separate reactors, $2\frac{1}{2}$ -in. diameter and 6-in. diameter of Monel and 2-in. diameter of nickel, were used for the pilot-plant fluorination studies. Two of these were for static-bed experiments and one for fluid-bed experiments.

The $2\frac{1}{2}$ -in. diameter Monel fluidized bed reactor was 6 ft in length, flanged at both ends, and topped by a 6-in.-diameter by 18-in.-high disengaging section. The bottom of the reactor consisted of a 60° cone section with the fluidizing gas entering through a $\frac{1}{2}$ -in.-diameter hole at the apex of the cone. Heat to the unit was supplied by semicylindrical, nichrome wire heaters with a total capacity of 7000 w. The desired temperature was maintained by connecting several of the heaters to a West automatic controller and the remainder to Variacs. Reactor skin temperatures were measured by thermocouples strapped to the outside wall of the reactor. Bed temperatures were measured by three thermocouples in a thermowell ($\frac{1}{2}$ -in.-diameter nickel tubing; closed end) which was inserted through the wall of the cone bottom and extended upwards into the reactor. Provisions were made for sampling the fluidized solids by the insertion of a sample line into the bed via a side arm welded onto the reactor 10 in. above the bottom flange. A screw feeder attached to the reactor at a point 2 ft above the bed was used for continuous feed runs. The feeder consisted of a $\frac{3}{4}$ -in. screw controlled by a variable-speed drive.

Static-bed experiments were performed in a 6-in.-diameter Monel fluorinator. This unit was 2 ft in height and flanged at both ends. The top flange contained a down-leg for introduction of gas, an outlet tube and a thermowell, all of nickel. Eight 1000-w calrod-type heaters controlled by Variacs supplied the necessary heat. A layer of nickel balls (of $\frac{1}{8}$ - to $\frac{1}{4}$ -in. diameter) was used in the bottom of the reactor to provide gas dispersion.

FIGURE 11
ADF FLUORINATION PILOT-PLANT EQUIPMENT

Additional static-bed studies were carried out in a 2-in.-diameter nickel reactor. This unit was 6 ft in length and flanged at both ends. The inlet gas was introduced through a baffled $\frac{3}{8}$ -in. line extending through the bottom flange. The baffle prevented powder from plugging the inlet line when there was no gas flow.

b. Fluorine Supply

Fluorine was supplied from high-pressure (400 psig) cylinders mounted in a steel, shielded enclosure. Figure 12 is a photograph of the fluorine enclosure, showing the cylinders and some of the valving which is operated through the steel door by extension handles. A manifold connected the cylinders to a medium-pressure surge tank which was filled with fluorine to a pressure of about 60 psig. This operation was accomplished by presetting the manifold valves (shown in the photograph) and then opening the main cylinder valves via extension handles which extend through a concrete wall surrounding the steel enclosure.

FIGURE 12
FLUORINE CELL

The fluorine was then passed through a Aveco Series 1194 control valve to a low-pressure surge tank which was maintained at a set constant pressure by a Taylor 66KFSS Transet Pressure Receiver and a 335RF111 Triact Controller. Fluorine flow was metered through calibrated orifices and through a thermal flow meter⁽¹⁵⁾ which furnished a constant recording of the flow rate. As a check, the fluorine flow could be determined by pressure drop of the medium-pressure surge tank (with a volume of 17.6 cu ft).

c. Off-gas Equipment

The tubing used throughout the system was either $\frac{3}{8}$ -in.-diameter or $\frac{1}{2}$ -in.-diameter nickel or Monel. Hoke #413 Monel diaphragm valves were used in places where hot streams of fluorine would be encountered. Imperial Teflon-diaphragm brass valves were used in cooler portions of the pipework. The off-gas lines from the reactors and auxiliary equipment were heat-traced with electrical heating wire to prevent condensation of volatile constituents. During static-bed tests the gas passed through a roughing filter consisting of a 1-ft section of $1\frac{1}{2}$ -in.-diameter nickel pipe packed with nickel wool to trap out entrained particulate. (This unit was not needed for the $2\frac{1}{2}$ -in. fluidized bed unit because of its integral disengaging section.) The gas then was passed through two filter units in parallel. These filters, equipped for flowback, were a bayonet-type of sintered Monel with 10-micron porosity (Micro-Metallic Co., Grade G).

After passing through the filters, the uranium hexafluoride in the off-gas was condensed in a 10-ft-long, 3-in.-diameter condenser containing $\frac{3}{4}$ -in. finned tubes through which trichloroethylene coolant was circulated. Later runs bypassed the above unit and the uranium hexafluoride was condensed in cold traps consisting of coils of $\frac{3}{4}$ -in. copper tubing immersed in a mixture of trichloroethylene and dry ice. These traps were valved and connected with flare fittings so they could be removed and weighed during a run to give an indication of the rate of uranium hexafluoride collection. In certain cases, the off-gas (primarily excess fluorine) was recycled to the inlet manifold by a Lapp Pulsafeeder remote-head diaphragm pump. Provisions were available for the addition of fresh fluorine during recycle operation. The pressure of the system was maintained at a set level by the bleed-off of a portion of the gas stream through a Aveco Series 1194 valve controlled by a Taylor Fullscope Recorder Controller. The recycling of fluorine considerably reduced overall fluorine consumption.

The exhaust gas passed through a process scrubber utilizing a concurrent stream of potassium hydroxide to remove fluorine and traces of uranium hexafluoride. The exit gas was then fed into the cell air-exhaust stream which passed through another caustic spray scrubbing system before release to the main building exhaust.

2. Pilot-plant Procedure

The procedure for the pilot-plant experiments involved charging material (see Table 15) to one of the reactors, starting a gas stream of nitrogen through the powder and bringing the unit up to the desired temperature. Fluorine was introduced at the desired concentration and the fluorination continued for the planned period of time.

Table 15

FLUID-BED DRYER CONDITIONS AND COMPOSITION OF DRYER PRODUCTS USED IN FLUORINATION STUDIES

Dryer Temp (C)	Feed Solution Composition			Dryer Runs (ZCP-)	Dryer Product Constituents ^a	Fluorination Runs (UZr-)
	F/Zr Mole Ratio	Free Acid (M)	Zirconium (M)			
240	4.5	0.7	1.2	44, 66, 74	ZrF ₄ ZrF ₄ ·H ₂ O(minor)	11-12, 15 34-37, 39-41, 104
300	4.5	0.7	1.2	42, 47, 50, 51, 60	ZrF ₄ (28%) ZrF ₄ ·H ₂ O (9%) ZrOF ₂ (57%)	5-10, 17, 19-27, 29 31-33, 38, 42-44
450	4.5	0.5	0.9	48	ZrO ₂ (90%) ZrOF ₂ (10%)	18
300	10	10	1.2	38	ZrF ₄	13-14, 16
300	6	10	3.6	73	ZrF ₄ ZrF ₄ ·H ₂ O	101-103
350	10	8.4	1.2	71	ZrF ₄ (75%) ZrOF ₂ (25%)	65
385	7.4	23	2.8	76	ZrF ₄ ZrOF ₂	106-111

^aPercentages shown are only approximate. Estimates made from X-ray and chemical analyses.

The velocity of the gas stream varied from 0.5 to 1.0 ft/sec at column conditions for the fluidized experiments. Static-bed tests were conducted at gas velocities of less than 0.1 ft/sec. Run durations ranged up to 12 hr with fluorination temperatures ranging from 450 C to 700 C. In the majority of the runs the bed height was approximately 12 in. The concentration of fluorine in the inlet gas stream was varied from 15 to 100 percent with nitrogen as the diluent.

Extent of uranium removal was determined by analysis of the final bed for uranium content. Samples of the inlet gas and outlet gas were taken to determine fluorine consumption. The gas was drawn into an evacuated bulb and analyzed for fluorine content by the potassium iodide-potassium thiosulfate titration procedure.⁽¹⁶⁾ This procedure was found to be unsatisfactory at fluorine concentrations above 30 percent and was superseded by a pressure-measurement technique. The revised sampling technique consisted of drawing a sample of the gas into an evacuated bulb

of known volume, which contained mercury. Reaction of the fluorine with mercury (upon shaking of the bulb) caused a decrease in pressure which permitted the calculation of the fluorine concentration.

Figure 13 is a photograph of the panel board containing most of the systems controls. After presetting certain valves in the process cell, the equipment could be operated from this control panel, thus avoiding the exposure of operating personnel to equipment containing fluorine at high temperatures.

FIGURE 13
FLUORINATION PANEL BOARD

3. Laboratory-scale Experimental Procedure

Preliminary laboratory-scale experiments were carried out in a fixed-bed apparatus consisting of a $\frac{3}{4}$ -in., vertical nickel tube heated by a furnace. A flow system was used. Preheated fluorine was admitted to

the tube through an orifice meter, and the uranium hexafluoride which was produced was collected in two cold traps in series. Later laboratory fixed-bed high-temperature tests were conducted in a 2-in.-diameter, vertical bomb reactor. Some of the experiments in this case involved batch injection of fluorine. The procedure consisted of charging the powder (250 to 600 g/charge) to the bomb, evacuating the bomb, heating to about 700 C, and adding fluorine to 750 or 1500 mm mercury pressure at the prescribed temperature. The fluorine was allowed to react for a specified time (5 to 15 min) and was then evacuated along with the reaction products through an aluminum oxide trap. The number of fluorine contacts was varied from one to six in these studies.

For the experiments with flowing fluorine, a down-leg was installed so that the fluorine was introduced at the bottom of the vessel and allowed to flow upward continuously through the charge. A helium purge was used during the heating up and cooling down period.

In the case of the high-temperature runs (near 700 C), the final bed was in the form of a hard cake which was sectioned and the separate sections analyzed for uranium content, or the entire cake was ground and analyzed.

B. Presentation and Discussion of Results

1. Effect of Fluorination Temperature on Uranium Removal from Various Dryer Products

The effect of fluorination temperature on uranium removal from various dryer products was investigated in the temperature range from 450 C to 700 C. Both fluid-bed and static-bed experiments were performed. The static-bed tests were conducted at high temperatures (>600 C) and are discussed in a subsequent section of this report. In general, higher fluorination temperatures gave greater uranium removal.

a. Experimental Results for Various Materials

Fluid-bed fluorinations of 300 C, low-acid dryer product, primarily zirconyl fluoride, showed increasing uranium removal with temperature: 42 percent at 450 C, and up to 91 percent at 600 C (see Table 16). The material fluorinated at 600 C was pretreated by fluorinating at 300 C for 4 hr. The pretreatment accounted for approximately 25 percent of the total uranium removal.

Results from fluorinations of 240 C, low-acid dryer products, primarily anhydrous and monohydrated zirconium tetrafluoride, also disclosed that increasing fluorination temperature improved uranium removal. A somewhat poorer removal, 69 percent at 600 C, was achieved

as compared with 82 percent at 525 C for the 300 C, low-acid dryer product. Utilizing a low-temperature fluorination pretreatment at 300 C followed by fluorination at 600 C, however, gave similar results for both materials, about 91 percent removal.

Table 16

EFFECT OF FLUORINATION TEMPERATURE ON URANIUM REMOVAL

Equipment: 2½-in.-diameter fluorinator
 Duration: 6 hr
 Gas Velocity: 0.5 ft/sec at column conditions
 Gas Composition: 100 percent fluorine
 Initial Uranium
 Concentration: 300 C Dryer product--1.0 weight percent
 240 C Dryer product--0.8 weight percent

Type of Dryer Product	Fluorination Temperature (C)	Final Uranium Concentration (w/o)	Uranium Removed (% of original)
300 C, low acid	450	0.58	42
"	525	0.18	82
"	600 ^a	0.09	91
240 C, low acid	450	0.34	58
"	600	0.25	69
"	600 ^a	0.06	92
"	675 ^b	0.008 ^c	>99
"	675 ^b	0.008 ^c	>99

^aMaterial prefluorinated at 300 C for 4 hr prior to 600 C fluorination.

^bCaked portion of bed.

^cLimit of X-ray spectrochemical method of analysis.

In two experiments noted in Table 16, in which the beds caked at an operating temperature of 600 C, temperature excursions took place in which a portion of the beds reached temperatures greater than 675 C. Samples of the caked portions of these beds showed residual uranium contents of less than 0.008 weight percent uranium (lower limit of detection by current X-ray spectrochemical analysis techniques⁽¹⁷⁾). This corresponds to a removal of greater than 99 percent of the uranium associated with a fuel alloy having a starting uranium content of two weight percent. These results prompted the investigation of high-temperature static-bed fluorinations as discussed in a later section of this report (page 69).

Poor uranium removal was encountered upon fluorination of material containing precipitated uranium tetrafluoride at 500 C in the fluid-bed fluorinator (see Figure 14): 50 and 61 percent at the end of 4 and 8 hr, respectively. Increasing the temperature to 600 C resulted in improved uranium removal, 92 and 96 percent for corresponding periods, although still below the desired 99 percent removal.

FIGURE 14
EFFECT OF FLUORINATION TEMPERATURE ON URANIUM REMOVAL FROM MATERIAL PRODUCED IN FLUID-BED DRYER AT 300 C
(Uranium precipitated as UF_4)

A few experiments were conducted where zirconium oxide was present in the dryer product. This material was present as the initial bed for the dryer, and was found in the feed to the fluorinator if dryer run time was insufficient to displace this material completely. The feed to the fluorinator then contained a layer of zirconium fluorides deposited over a core of zirconium oxide. Dryer operation at 450 C also produced zirconium oxide.

Fluorination for 8 hr at 500 C of material dried at 450 C (primarily zirconium dioxide) yielded 73 percent uranium removal. Fluorination under the same conditions of material consisting of a layer of 240 C dryer product over a core of zirconium dioxide removed 96 percent of the uranium in the coating.

b. Discussion

The differences noted in the fluorinating characteristics of the different dryer products is probably related to their composition. (Chemical analyses of the 240 C and 300 C dryer products are presented in Table 17.) The 240 C, low-acid dryer product consists mainly of anhydrous and monohydrated zirconium tetrafluoride, whereas the 300 C, low-acid dryer product consists mainly of zirconyl fluoride. From the relative uranium removal noted for these two dryer products, it may be postulated that the presence of water in the 240 C dryer product hindered uranium removal, whereas the reaction of fluorine with the zirconyl fluoride produced at 300 C may have generated high particle temperatures which more readily facilitated uranium removal. The prefluorination at 300 C seemed to remove the effects which caused differences in behavior. One explanation is that the water in the monohydrated material was removed during the fluorination at the lower temperature, leaving the powder more porous.

Table 17

COMPOSITION OF DRYER PRODUCTS BEFORE AND AFTER
HYDROFLUORINATION PRETREATMENT

Material	Chemical Analyses			F/Zr Mol Ratio	Material Volatile at 450 C	
	Zirconium (%)	Fluoride (%)	Oxygen (%)		HF (%)	H ₂ O (%)
300 C dryer product	54.8	30.9	6.5	2.71	1.5	0.4
Same, after hydro- fluorination	49	41.3	1.70	4.05	3.6	0.11
240 C dryer product	47	40.6	4.03	4.15	3.4	1.8
Same, after hydro- fluorination	46	43.4	1.03	4.53	3.3	0.43
<u>Theoretical Compositions</u>						
ZrOF ₂	62.7	26.2	11.1	2.00	-	-
ZrO ₂	74.1	-	25.9	-	-	-
ZrF ₄	54.5	45.5	-	4.00	-	-

The results obtained on fluorination of material containing precipitated uranium tetrafluoride indicated that this method of preparing powder with uranium present as discrete particles within the zirconium fluoride matrix was not completely successful. The results obtained from fluorinations of material containing zirconium oxide may be related to two possible effects. The more favorable removal achieved from material consisting of a layer of zirconium and uranium fluoride deposited on the core of zirconium oxide could be due to the relatively short path required for diffusion of fluorine and/or uranium hexafluoride. On the other hand, the highly exothermic reaction between zirconium oxide and fluorine could cause excessively high particle temperatures, resulting in sintering and trapping of uranium within the particles in some cases, particularly when the particle consisted almost entirely of a reactive type of zirconium oxide.

2. Effect of Pretreatment of Dryer Products

In an attempt to increase the uranium removal from the solids produced in the fluid-bed dryer, the materials were subjected to various pretreatments prior to fluorination. These included hydrofluorination, heating to remove volatiles, and other treatments which are discussed below. The change in compositions of these materials as a result of hydrofluorination is presented in Table 17.

a. Effect of Hydrofluorination

The hydrofluorination pretreatment of material prepared at 240 C apparently had a beneficial effect (see Table 18); uranium removal at 600 C increased from 69 percent to 89 percent. This pretreatment applied to material dried at 300 C apparently had a deleterious effect since uranium removal decreased from 78 to 55 percent upon fluorination at 525 C. Since the chemical composition of both the 300 C and 240 C materials after hydrofluorination were quite similar, their chemical reactivity may have varied because of more subtle effects, such as crystallite size or structure. The poor behavior of the 300 C material could also be attributable to sintering, since some heat of reaction was evident during hydrofluorination.

b. Effect of Preheating Dryer Product

A 7-hr preheat in nitrogen at 600 C, which was expected to volatilize residual water and hydrogen fluoride from the dryer product and leave the material more porous, gave negative results (see Table 19): 89 percent uranium removal after 8 hr of fluorination at 500 C, as compared with 98 percent without the heating step. However, the 4-hr samples in both cases showed equivalent uranium removals, 88 percent. Sintering may have occurred during the heating step and affected only a portion of the uranium.

The dryer product in this case was prepared at 240 C; this produced a matrix consisting primarily of zirconium tetrafluoride and a minor fraction of monohydrate.

Table 18

EFFECT ON URANIUM REMOVAL OF HYDROFLUORINATION
PRETREATMENT PRIOR TO FLUORINATION

Equipment: 2 $\frac{1}{2}$ -in. diameter fluorinator
Gas Composition: 100 percent F₂
Gas Velocity: 0.5 ft/sec
Run Duration: 6 hr

Run No.	Starting Material	Fluorination Temperature (C)	Uranium Concentration		Uranium Removed (% of Original)
			Initial (w/o)	Final (w/o)	
UZr-33	300 C dryer product	525	1.0	0.22	78
UZr-38	Same after hydro-fluorination	525	1.0	0.45	55
UZr-36	240 C dryer product	600	0.8	0.25	69
UZr-41	Same after hydro-fluorination	600	0.8	0.09	89
UZr-37	Same after hydro-fluorination	525	0.8	0.11	86

Table 19

EFFECT ON URANIUM REMOVAL OF PREHEATING DRYER
PRODUCT PRIOR TO FLUORINATION

Equipment: 2 $\frac{1}{2}$ -in. diameter fluorinator
Starting Material: 240 C, low-acid dryer product
Initial Uranium Concentration: 1.27 w/o
Fluorination Temperature: 500 C
Gas Composition: 15 percent fluorine in nitrogen
Gas Velocity: 1.0 ft/sec at column conditions

Fluorination Run No.	Treatment	Percent of Original Uranium Removed	
		After 4 hours	After 8 hours
UZr-15	Preheated in nitrogen at 600 C for 7 hours	88	89
UZr-11	None	88	98

c. Effect of Additives

An attempt was made to improve uranium removal by the addition of substances to the feed solution that would volatilize during fluorination. This was expected to increase the porosity of the particles and augment uranium removal; however, as noted in the laboratory-scale tests below, results were generally unfavorable.

(1) Silica

The addition of silica to the feed was without success as it volatilized during the drying step.

(2) Carbon

A sample containing about 2.0 percent uranium and 10 moles of carbon (added as dextrose) per mole of uranium was fluorinated for 2 hr at 600 C. Initially, 20 moles of carbon were added to the liquid feed per mole of uranium, but apparently about half of the carbon oxidized (and was eliminated) during the drying step. The results showed about 87 percent removal of uranium and about 96 percent removal of carbon. Thus, no improvement in uranium removal as a result of carbon addition was obtained.

(3) Sulfate

The use of sulfate as an additive was suggested by the work of Colvin,⁽¹⁸⁾ in which very porous calcium fluoride was produced by fluorinating calcium sulfate. Laboratory fluorination experiments were made on two samples containing three percent uranium and 24 and 10 moles of sulfur (as sulfate) per mole of uranium, respectively. The solids were fluorinated for 2 hr at 600 C with 100 percent fluorine. The results showed about 92 percent removal of uranium for both samples. This uranium removal was slightly better than realized with carbon addition, but was not sufficiently improved to warrant further study.

d. Effect of Metal Impurities

Since laboratory-scale fluorination of solids prepared in the laboratory in polyethylene equipment frequently showed greater uranium removal than those prepared in the fluid-bed pilot plant, a study was made of the effect of metal impurities present as a result of corrosion of the pilot-plant Monel dissolver and the stainless steel feed tank. Presence of such impurities might inhibit volatilization of trace amounts of uranium since under certain conditions uranium forms complexes from which the uranium can be volatilized only with difficulty. Such a condition is known to exist in the case of uranium and potassium.⁽¹⁹⁾ Copper, nickel and

chromium salts were added to the uranium-zirconium-fluoride solutions in concentrations equal to five times that of the uranium. Results of this series of fluorinations made at 600 C on materials containing up to two percent uranium showed little or no effect of the impurity additions.

3. Effect of Duration of Fluorination

Several experiments were conducted to study the effect of the fluorination period on uranium removal. In one case, the data were obtained by taking grab samples of the solids from the fluorinator at 30-min intervals for the first 2 hr and then again after 4 and 8 hr. This test was a 500 C fluorination of 300 C, low-acid dryer product. The fluidizing gas stream consisted of 15 percent fluorine in nitrogen. Results summarized in Figure 15 show a relatively abrupt decrease in the rate of uranium removal after 4 hr with the 4- and 8-hr results being nearly identical.

FIGURE 15
EFFECT OF DURATION OF FLUORINATION
ON URANIUM REMOVAL

Conditions:

Run No. : UZr-29
 Gas Composition : 15% F₂ in N₂
 Gas Velocity : 1.0 ft/sec
 Temperature : 500 C
 Starting Material: 300 C, low-acid dryer product

Table 20 shows similar data from a series of runs in which various materials were exposed to a stream of 100 percent fluorine for various times. Essentially no additional uranium removal was effected by runs over extended periods; the major fraction of uranium is apparently removed within the first few hours. This resistance to uranium removal could be due to a sintering-type action which hinders diffusion of the reactant, fluorine, into the particles or prevents the gaseous product, uranium hexafluoride, from escaping. It is also possible that the uranium removal occurs via two mechanisms, the first giving a high rate and the second a much slower rate.

Table 20

EFFECT OF FLUORINATION PERIOD ON URANIUM REMOVAL

Equipment		2½-in -diameter fluorinator				
Gas Composition		100 percent F ₂				
Gas Velocity		0.5 ft/sec				
Run No	Starting Material	Fluorination Temperature (C)	Time of Fluorination (hr)	Uranium Concentration		Uranium Removed (% of original)
				Initial (w/o)	Final (w/o)	
UZr-33	300 C Dryer Product	525	6	1.0	0.22	78
			12	1.0	0.20	80
UZr-38	Same after hydro- fluorination	525	2	1.0	0.41	59
			4	1.0	0.34	66
			5	1.0	0.45	55
UZr-35	240 C Dryer Product	450	4.5	0.8	0.38	53
			6.0	0.8	0.34	58
UZr-36	240 C Dryer Product	600	4.0	0.8	0.23	71
			6.0	0.8	0.25	69
UZr-37	Same after hydro- fluorination	525	3.0	0.8	0.13	84
			5.0	0.8	0.11	87

4 Effect of Gas Velocity

Experiments were performed to determine the effect of fluidizing gas velocity on uranium removal. The solid feed material for these runs contained a core of zirconium oxide (the starting bed material for the dryer operation) amounting to about 45 weight percent. The experiments consisted of two successive 4-hr fluorinations at 500 C using 15 percent fluorine in nitrogen as the fluidizing gas stream. Tests were made over a range of gas velocities, 0.19 ft/sec (a static-bed condition) to 0.95 ft/sec which is about four to five times the minimum fluidizing velocity for the material used.

Data indicate velocity was important only in that higher velocities introduced more fluorine for a given period of time. Uranium removal,

for the period where removal rate was high, was proportional to the amount of fluorine passed through the bed (see Table 21 and Figure 16).

Table 21

EFFECT OF GAS VELOCITY ON URANIUM REMOVAL

Equipment: 2½-in.-diameter fluorinator
 Fluorination Temperature: 500 C
 Inlet Gas Composition: 15 percent fluorine in nitrogen
 Initial Uranium Concentration: 0.75 percent

Fluorination Run No.	Gas Velocity (ft/sec)	Uranium Concentration After Quantity of Fluorine Passed (w/o)			Condition of Bed ^a
		7.5 cu ft	8.8 cu ft	17.4 cu ft	
UZr-29	0.95	0.51	0.46	0.21	Slugging fluidization
UZr-25	0.57	-	-	0.24	Well fluidized
UZr-26	0.27	-	0.55	-	Upper part fluidized, velocity just above minimum for fluidization
UZr-27	0.19	0.61	-	-	Static Bed

^aAs determined in glass column with nitrogen as fluidizing gas

FIGURE 16

RESIDUAL URANIUM CONTENT AS A FUNCTION OF QUANTITY OF FLUORINE PASSED THROUGH BED AT VARIOUS GAS VELOCITIES

Equipment : 2-1/2-in.-diameter fluorinator
 Starting Material : 300 C, low-acid dryer product (ZCP-51)
 Inlet Gas Composition : 15% F₂ in N₂
 Fluorination Temperature : 500 C

At the low gas velocities, comparatively little uranium was removed in 8 hr because of the small amount of fluorine introduced. In each case the first 4 to 6 cu ft of fluorine fed to the reactor were completely consumed by reaction with the residual oxygen or water with little or no release of uranium hexafluoride. This was determined by analyses of the exit gas. Calculations based on the known oxygen content, considering approximately sixty percent of the coating to be zirconyl fluoride, show that if the efficiency of fluorine utilization was 100 percent, approximately 12 cu ft of fluorine was required to convert the materials to zirconium tetrafluoride. However, the plot of Figure 16 shows uranium is being removed at a reasonable rate after the first 4 cu ft of fluorine was passed, indicating the competing reactions of fluorine with both zirconium and uranium compounds are progressing simultaneously.

5. Effect of Particle Size

Investigations were made into the removal of uranium from various-sized particles. Fluorinations of normal dryer products and those containing a core of zirconium oxide disclosed in general that the percentage of uranium removed from a particle did increase as particle size decreased, as discussed below.

a. Material Containing Zirconium Dioxide Core

Results of a 500 C fluorination of 300 C dryer material deposited on a core of zirconium oxide are presented in Table 22. Samples were taken of the starting bed and at various times during the fluorination period. Each sample was sieved and the separate fractions analyzed for uranium. A greater percentage of the uranium was found to have been removed from the smaller-sized particles. After a 2-hr exposure at 500 C, uranium removal ranged from 51 percent for the -20 +40 mesh fraction to about 83 percent for the -100 +200 mesh fraction. Corresponding 8-hr results were 76 and 91 percent. The bed composite sample showed an average removal of 86 percent for the 8-hr period.

The penetration of fluorine into the particles equivalent to the uranium removed was calculated from a knowledge of the uranium content of the deposited layer (1.25 weight percent) and the overall uranium content of the particles before and after fluorination. Calculated values of the shell thickness based on the assumption of a sphere of zirconium oxide surrounded by a shell of uranium-bearing material ranges from 80 microns for the plus 20 mesh particles (average diameter $\sim 1000 \mu$) to 24 microns for the -100 +200 mesh size (average diameter 112μ). For the initial 2-hr fluorination period, calculated penetration ranged from 18 to 25 microns (see Figure 17). This means a greater percentage of the uranium was removed initially from the smaller-sized particles. As the fluorination period lengthened, the rate of penetration of fluorine into and/or uranium hexafluoride

out of the particle decreased and the larger sized particles seemed to show greater penetration. If real, the difference in behavior of the various particle sizes could be related to the manner in which the different sizes are formed in the dryer.

Table 22

EFFECT OF PARTICLE SIZE ON URANIUM REMOVAL FROM
MATERIAL HAVING A ZIRCONIUM DIOXIDE CORE

Fluorination Temperature: 500 C
Inlet Gas Composition: 15 percent fluorine in nitrogen
Inlet Gas Velocity: 1.0 ft/sec
Starting Material: 300 C, low-acid dryer product (ZCP-51)
Run Number: UZr-29

Mesh Fraction Size	(w/o)	Ratio of Core to Particle Diameter	Thickness of Coating ^a (μ)	Initial Uranium Concentration (w/o)	Uranium Removal (%)		
					2-hr product	4-hr product	8-hr product
+20	1.9	0.840	80	0.51	-	-	72.5
-20+40	13.1	0.832	52	0.53	51	-	76.5
-40+60	37.2	0.796	34	0.62	64.5	71.0	82.3
-60+100	37.9	0.718	28	0.79	74.8	77.2	87.4
-100+200	9.9	0.568	24	1.02	83.3	-	91.2
Composite Bed Sample	100.0	-	-	0.75	68	-	85.9

^aBased on assumption of two concentric spheres, zirconium oxide surrounded by a shell of zirconium-uranium fluorides having a uranium concentration of 1.25 w/o.

FIGURE 17

PARTICLE PENETRATION EQUIVALENT TO URANIUM REMOVAL
AS A FUNCTION OF PARTICLE SIZE AND TIME

Equipment : 2-1/2-in. -diameter fluorinator.
Run No. : UZr-29
Starting Material: 300 C, low-acid dryer product (ZCP-51).
Fluorination Temperature: 500 C
Gas Velocity: 0.95 ft/sec at column conditions.
Inlet Gas Composition: 15% F₂ in N₂.

b. Material without Zirconium Dioxide Core

Additional studies were made of the effect of particle size on uranium removal, utilizing material which contained essentially no core, i.e., the dryer was operated for sufficient time to displace the zirconium oxide starting bed. The results of these runs are shown in Table 23. In general, it may be observed that at high fluorination temperatures (>500 C) the uranium removal was increased as particle size decreased. This was noted for both 300 C dryer product and for 240 C dryer product. At a fluorination temperature of 450 C no effect of particle size was evident. Hydrofluorination of the dryer products negated particle size effect for 240 C material and seemed to minimize the effect for 300 C material.

Table 23

EFFECT OF PARTICLE SIZE ON URANIUM REMOVAL

Inlet Gas: 100% F_2
 Fluidizing Velocity: 0.5 ft/sec
 Duration of Fluorination: 6 hr
 Initial Uranium Content: 300 C dryer product, 1.00 weight percent
 240 C dryer product, 0.80 weight percent

Run No.	Starting Material Dryer Temperature (C)	Fluorination Temperature (C)	Uranium Removed in Following Mesh Sizes (% of original)		
			-40+60	-60+100	-100+200
UZr-31	300	450	41 (28) ^c	-	43 (10) ^c
UZr-32	300	525	77 (65)	-	85 (25)
UZr-33	300	525	74 (60)	80 (46) ^c	89 (30)
UZr-45 ^a	300	600	94 (101)	-	96 (38)
UZr-35	240	450	54 (38)	-	55 (13)
UZr-36	240	600	55 (36)	81 (42)	-
UZr-40 ^a	240	600	88 (92)	-	95 (35)
UZr-37 ^b	240	525	86 (80)	88 (50)	85 (26)
UZr-38 ^b	300	525	62 (46)	69 (32)	70 (18)

^aPretreated with F_2 at 300 C before fluorination.

^bStarting beds pretreated with HF before fluorination.

^cNumber in parentheses refers to penetration in microns of fluorine into and/or UF_6 out of particles assuming a linear penetration.

The penetration of fluorine into the particles calculated from the uranium content of the particles before and after fluorination is also shown in Table 23. The values for similar-sized particles are in general higher than those observed in Figure 17, for which the starting material had a core of zirconium oxide.

6. Reproducibility of Results

In order to determine the reproducibility of fluid-bed fluorination experiments, a batch of dryer product was blended in a twin-shell blender and then divided into four fractions, each of which was separately fluorinated for 8 hr at 600 C with 15 percent fluorine in the fluidizing gas. The 4- and 8-hr values for uranium removal (see Table 24) showed excellent agreement, 91.8, 91.6, 90.9, and 91.2 percent, and 95.0, 92.5, 92.8, and 93.1 percent, respectively. The plateau effect noted previously was in evidence in these tests.

Table 24

FLUORINATION REPRODUCIBILITY EXPERIMENTS

Equipment:	2½-in.-diameter fluorinator
Fluidizing Gas Velocity:	~1 ft/sec
Fluidizing Gas Composition:	15 percent fluorine in nitrogen
Run Duration:	8 hr
Fluorination Temperature:	600 C
Feed Material:	ZCP-50, 300 C, low-acid dryer product

Fluorination Run No.	Uranium Concentration of Bed (w/o)			Percent Uranium Removed After Fluorination Time of	
	Before Fluorination	After 4-hr Fluorination	After 8-hr Fluorination	4 hr	8 hr
UZr-21	2.18	0.18	0.11	91.8	95.0
UZr-22	2.26	0.19	0.17	91.6	92.5
UZr-23	2.08	0.19	0.15	90.9	92.8
UZr-24	2.17	0.19	0.15	91.2	93.1

7. Microscopic Examination of Particles

A microscopic examination was made of dryer products and fluorinated materials to attempt to ascertain what happens to the physical structure of the particles during fluorination. A 300 C dryer product was fluorinated for 12 hr at both 500 C and 600 C (Runs UZr-5 and UZr-8). Samples of the dryer product and fluorinated residues were mounted in plastic and polished. Microphotographs of these are shown in Figure 18. The cores of these particles were apparently preferentially removed during fluorination at the higher temperatures (Figure 18c). Since the particles originally contained a zirconium oxide core, the reaction of fluorine with the oxide might produce a temperature high enough to volatilize some of the zirconium tetrafluoride, which has vapor pressures of 0.2, 6 and 70 mm Hg at 600, 700, and 800 C, respectively. Another explanation for the hollow spheres might be core (oxide) decrepitation during fluorination.

FIGURE 18
PHOTOMICROGRAPHS OF FLUID-BED DRYER PRODUCTS

Particle Size: -20 +40 mesh
Magnification: 20 X
Dryer Temperature: 300 C

(a) Run ZCP-42, 16 hours operation, ZrO_2 starting bed

PHOTOMICROGRAPHS OF FLUID-BED FLUORINATION PRODUCTS

Particle Size: -20 +40 mesh
Magnification: 26 X

(b) Dryer product from ZCP-42, fluorinated 12 hours at 500 C

(c) Dryer product from ZCP-42, fluorinated 12 hours at 600 C

Photomicrographs of precipitated uranium tetrafluoride feed material taken before and after fluorination at 500 C are shown in Figure 19. The fluorinated particles showed no obvious structural change and appeared to be nonporous and crystalline. Uranium removal in this case was poor.

FIGURE 19
PHOTOMICROGRAPHS OF PRECIPITATED URANIUM
DRYER PRODUCT - FLUORINATED RESIDUE

Particle Size: -20 +40 mesh

Magnification: 20 X

(a) Dryer product from Run ZCP-38, 75 hours operation, CaF_2 starting bed.

Magnification: 26 X

(b) Dryer product from Run ZCP-38, fluorinated 8 hours at 500 C

8. Surface Area Measurements

Measurements of surface area were made by the nitrogen-adsorption method on fluid-bed dryer products and fluorination products to determine if there were a relationship between the expected decrease in surface area due to possible sintering of the particles during fluorination

and the degree of uranium removal. The dryer products had uranium contents ranging from 2 to 4 weight percent. The data presented in Table 25 indicate there is a 3- to 25-fold decrease in surface area during fluorination; however, no direct correlation between surface area and degree of uranium removal could be determined from the available data.

Table 25
SURFACE AREA MEASUREMENTS ON FLUID-BED
DRIED AND FLUORINATED MATERIAL

(Fluorination Temperature: 600 C)

Type of Dryer Product		Fluorination Time (hr)	Initial Uranium Concentration (w/o)	Surface Area (sq m/g)		Uranium Removal (%)
Drying Temperature (C)	F/Zr Mole Ratio			Before Fluorination	After Fluorination	
300	10 ^a	8	2.16	2.6	0.1	95
350	3.5	6	2.38	3.0	1.2	92
300	3.5	12	4.5	4.8	0.9	98

^aContained precipitated UF₄.

9. High-temperature Static-bed Fluorinations

Quantitative separation of uranium from uranium fluoride-zirconium fluoride matrices had been achieved from caked beds at high temperatures (see Table 16), so the effects of fluorination temperatures in excess of 600 C were investigated.

One procedure consisted of an attempt to produce high temperatures of individual particles while maintaining a relatively low overall bed temperature. A screw feeder was used to introduce the dryer product into a bed of inert calcium fluoride fluidized with fluorine at 500 C or 600 C. It was expected that the reaction of the feed with the fluorine gas stream would produce individual particle temperatures significantly higher than the bed temperature and for a time sufficiently long to achieve complete uranium removal. The system performed satisfactorily at temperatures near 500 C, but uranium removal was not significantly enhanced. Difficulties with cake formation at higher temperatures (near 600 C) even with high fluidizing velocities forced the abandonment of this technique.

Temperatures to 700 C were then used in the application of a fixed-bed fluorination step to the process. Experiments were carried out utilizing a bench-scale, 2-in.-diameter, vertical reactor and on a pilot-plant-scale with a 6-in. diameter by a 2-ft-tall unit and a 2-in.-diameter by 6-ft tall unit designed to investigate the effect of bed height and the pressure drop across the caked beds.

a. Conditions

The bench-scale work compared two types of fluorine contacting: batch exposures to fluorine and continuous flow. In the batch system, fluorine was introduced above the powder, allowed to react, and the gaseous products were then evacuated. This cycle was repeated a number of times according to plan. In the flowing system, fluorine was introduced at the bottom and allowed to flow upward through the bed.

The starting material for these runs was prepared from a high-acid feed dried at 350 C. Hydrofluorination at 450 C was used (in Run ZCP-71 HF) to reduce its oxygen and water content. Variables investigated included amount of fluorine, duration of fluorination, and temperature of fluorine introduction.

The variables investigated in the pilot-plant units included the amount of fluorine, duration of fluorination, temperature of fluorine introduction, gas velocity, bed height, and the determination of pressure drop across the caked beds. The materials tested were hydrofluorinated dryer products.

b. Results

Summaries of the bench-scale and pilot-plant static-bed fluorinations are presented in Table 26 and 27, respectively. In order to evaluate the results of a run, grab samples taken from several portions of the caked (sintered) final bed were analyzed for uranium. These samples were designated as top, middle, and bottom, corresponding to the portion from which they were obtained. Analysis of a composite sample from an entire bed which was crushed and blended agreed well with the average of the grab samples (see Table 27, Run UZr-106).

(1) Amount of Fluorine and Duration of Fluorination

The quantity of fluorine necessary to assure quantitative removal of uranium from the uranium-zirconium-fluoride mixtures was found to be dependent not only on the amount of uranium present but also on the oxygen content of the feed materials. If the oxygen is present as oxides or oxyfluorides of zirconium, one mole of fluorine will be required for every gram-atom of oxygen, assuming conversion of these compounds to zirconium tetrafluoride. The stoichiometric fluorine requirements were based on oxygen content of the feed material rather than on the uranium content, since the fluorine requirements for uranium were small compared to that required for oxygen removal.

It is seen from the bench-scale experiments (see Table 26) that the uranium removal increased as the mole ratio of fluorine to oxygen increased. Run BF-5, utilizing less than stoichiometric amounts

of fluorine, exhibited no detectable uranium removal, indicating the fluorine was probably completely utilized in converting the zirconium oxygen-bearing compounds to the tetrafluoride. In all cases where incomplete uranium removal was noted, depletion of uranium occurred at one end of the cake and the uranium concentration increased at the other end to a concentration above that in the starting material (see especially Runs 8 and 9). This indicates that as uranium hexafluoride was being transported through the bed it was subsequently reacting with constituents of the bed, and being redeposited. The uranium concentration always increased in the direction away from the fluorine inlet.

Table 26

SUMMARY OF BENCH-SCALE HIGH-TEMPERATURE STATIC-BED EXPERIMENTS

Equipment: 2-in.-diameter x 12-in.-long nickel tube
 Starting Material: ZCP-71 HF (Hydrofluorinated dryer product),
 0.21 w/o uranium,
 ~1.0 w/o oxygen
 Inlet Gas: 100% fluorine

Run No.	Wt of Charge (g)	Total Fluorination Time (hr)	Number of Exposures ^{c,d}	$\frac{\text{gF}_2}{\text{g powder}}$	Mole Ratio F ₂ /O	Portion of Cake Sampled	Residual Uranium Conc (w/o)	Uranium Removal (% of original)
BF-5	500	0.75	3	0.014	0.58	Top Bottom	0.23 0.20	0
BF-8	250	0.5	6	0.053	2.2	Top Bottom	0.02 0.64	-
BF-6	250	1.5	6	0.053	2.2	Top Bottom	0.04 0.17	50
BF-7 ^a	250	1.5	6	0.053	2.2	Top Bottom	0.04 0.27	26
BF-9	250	0.75	flowing	0.032	1.3	Top Bottom	0.68 0.11	-
BF-10	250	0.50	flowing	0.080	3.3	Top Bottom	0.16	24
BF-13	500	3.1	flowing	0.14	5.8	Top Bottom	0.10 0.033	69
BF-11 ^b	250	1.0	flowing	0.252	10	Top Bottom	<0.008 <0.008	>96
BF-12	250	2.0	flowing	0.316	13	Top Bottom	0.023 0.014	92

^aF₂ introduced at room temperature.

^bF₂ introduced when temperature of charge reached 300 C.

^cSeparate exposures of 15-min duration except Run 8 in which 5-min exposure was used.

^dIn batch system F₂ introduced above powder; in flowing system F₂ introduced at bottom of reactor and allowed to flow upwards through the powder.

Table 27

SUMMARY OF PILOT-PLANT HIGH-TEMPERATURE STATIC BED EXPERIMENTS

		Feed Material		ZCP 73HF Dryer Product 0 62 w/o uranium		0 76 w/o oxygen					
				ZCP-74HF Dryer Product 1 08 w/o uranium		1 24 w/o oxygen					
		Inlet Gas		ZCP 76HF Dryer Product 0 56 w/o uranium		0 63 w/o oxygen					
		100% F ₂									

^aF₂ introduced at room temperature all others between 500 C and 600 C^bApproximately 1/3 of this F₂ added after bed temperature reached 650 C^cBed shrunk approximately 35% during run due to sintering of powder^dAnalysis by wet chemical analysis all others X ray spectrographic analysis^eThese runs were made in the 2-in.-diameter unit all others in 6-in. diameter unit^fFeed material heated at 450 C for 4 hours before hydrofluorination pretreatment

Much better uranium removal occurred in the flowing system experiments where higher mole ratios of fluorine to oxygen were used. The best removal in this series, 96 percent in one hour, was achieved using ten times the stoichiometric amount of fluorine (see Run BF-11). In contrast, Runs BF-12 and 13, in which large excesses of fluorine for 2- and 3.1-hour periods were employed, exhibited poor removals. The main difference between these runs and BF-11 was the temperature at which fluorine was introduced: room temperature during BF-11, and 700 C for the other runs.

The results of the first three runs in the 6-in.-diameter fluorinator were very favorable (see Table 27). The uranium removal ranged from 97 to greater than 99 percent. In one case, a duration of only 1½ hr at temperatures above 650 C was required to achieve the desired

results (Run UZr-101). The amount of fluorine used ranged from 3.1 times stoichiometric to 19 times stoichiometric, as based on oxygen analysis of the starting material. Subsequent runs using several different dryer products gave somewhat poorer results.

Refluorination of the final bed from one of the runs increased the uranium removal from 95 to only 97 percent, a result indicating that the duration of fluorination has only a slight effect on uranium removal. A run of 8-hr duration showed little or no improvement over the shorter runs noted.

Fluorination at these high temperatures resulted in the formation of a hard cake which was rather difficult to remove from the fluorinator vessel. Actual application of this technique to a full-scale process would probably require the use of a disposable fluorinator which might also be used as a waste-storage container. The design and economics of such a unit have been investigated and are presented in the appendix of this report.

(2) Bed Height and Gas Velocity

In view of the design concept of a large disposable fluorinator, the effect of bed height was investigated. The runs in the 2-in.-diameter by 6-ft-tall reactor indicated this variable had little effect on uranium removal. Beds of 2.5 ft and 4.5 ft (Runs 107 and 109, respectively) were used as compared to 1-ft deep beds in the 6-in. column.

Analyses of the exit gas for fluorine indicated that the concentration increased from zero to a plateau of 80 to 90 percent in the first one or two hours, indicating the major portion of the reaction had occurred during this period. Fluorine efficiency during the initial stages appeared to be improved by increased bed height, as expected.

No pronounced effect of gas velocity was noted in the range from 0.05 to 0.10 ft/sec. However, Run UZr-107, which utilized the lower superficial velocity, did show a higher gradient of uranium concentration in the residual caked bed. The gradient effect was mentioned previously in the bench-scale static-bed tests.

The initial pressure drop across the static beds was about 3 in. of mercury for the flow rates stated. As the runs progressed and the cake formed, the pressure drop decreased. This may have been caused by channelling of the gas and also by the fact that the bed height decreased about 35 percent during the course of the deep-bed runs, due to sintering of the solids.

c. Discussion

A comparison of bench-scale and pilot-scale runs shows only minor differences in behavior. Greater uranium removal was achieved in the pilot plant for similar stoichiometric ratios of fluorine to oxygen.

The differences in uranium removal noted from different dryer products under similar fluorinating conditions must be attributable to the characteristics, both chemical and physical, of the dryer product. Table 28 describes the several dryer products and summarizes the results of the static-bed experiments conducted with each type. The material which showed consistently good uranium removal was prepared at 300 C from high-acid, high-zirconium feed solution. This dryer product, as produced, consisted primarily of zirconium tetrafluoride and zirconium tetrafluoride monohydrate. The hydrofluorination pretreatment which followed removed the bulk of the water. The 240 C, low-acid, low-zirconium material also was of similar composition, but subsequent hydrofluorination and fluorination gave unsatisfactory results. Oxygen analysis of fluorinated residues show a lower residual oxygen content where the best uranium removal was achieved. Dryer products which originally contained zirconyl fluoride gave ambiguous and generally poorer results upon fluorination. This was possibly due to the hydrofluorination pretreatment since similar results were noted in the fluid-bed work. High temperature is needed for complete uranium separation, but if sintering is too severe, some of the uranium may be "trapped" within the particles, thus preventing quantitative removal.

Table 28

CHARACTERISTICS OF DRYER PRODUCTS FLUORINATED IN STATIC-BED HIGH-TEMPERATURE EXPERIMENTS

Run No	Feed to Dryer			Drying Temp (C)	Dryer Product Composition				Composition after Hydrofluorination ^a				Composition after Fluorination at 650-700 C	
	Zirconium (M)	Free Acid (M)	F/Zr Mole Ratio		O (w/o)	F (w/o)	Zr (w/o)	Approx Composition	O (w/o)	F (w/o)	Zr (w/o)	U (w/o)	O (w/o)	U (w/o)
ZCP-71	1.2	8.4	10	350	-	32.4	48	ZrF ₄ (75%) ZrOF ₂ (25%)	~1.0	44.4	48	0.21	-	-
-73	3.6	10	6	300	2.05	42.4	51.0	ZrF ₄ ZrF ₄ ·H ₂ O	0.76	44.0	50.0	0.62	0.25	0.008
-74	1.2	0.7	4.5	240	3.63	41.2	50	ZrF ₄ ZrF ₄ ·H ₂ O	1.24	-	-	1.08	0.46	0.03
-76	2.8	23	7.4	385	2.29	41.3	49.2	ZrF ₄ (80%) ZrOF ₂ (20%)	0.63	44.2	49.1	0.56	0.62	0.033

^aFour hours with HF at 450 C

10. Corrosion

Scaling of the 3-in.-diameter Monel reactor had been observed after each fluorination run, with higher temperatures producing greater quantities of corrosion product. The scaling appeared to be most severe

in the vapor phase above the bed. This behavior is similar to the high vapor phase attacks experienced in volatility fused salt process work.⁽²⁰⁾ Exploratory corrosion data were obtained by inserting corrosion coupons into the fluid-bed fluorinator during the early runs. The coupons were supported on a $\frac{1}{4}$ -in. nickel tube at two different elevations within the bed. The support tube also served as a corrosion specimen for evaluating both bed and vapor-phase attack. A total of eight 4-hr runs were made, five at a bed temperature of 500 C, the balance at 600 C. The material being fluorinated consisted primarily of zirconium tetrafluoride and zirconium oxyfluoride with small amounts of uranium tetrafluoride and uranium oxyfluoride. The uranium content of the initial charges varied from three to six weight percent. In all these runs the fluidizing gas was 15 percent fluorine in nitrogen.

a. Corrosion of Nickel Specimens

The coupon support tube (nickel) was removed and examined for dimensional change and subsurface corrosion evaluation. The dimensional change data, together with results of intergranular attack, are depicted graphically in Figure 20a.

The changes of dimensions were procured by taking micrometer readings of the diameter of the support tube after corrosion products had been removed. Removal was effected by soaking in water plus rubbing lightly with steel wool. The tube showed a very low attack in the area of the fluid bed, which is estimated to reach a maximum height of about 18 in. The most severe metal loss occurred at elevations of 35 and 47 in.

Specimens 2 and 3 consisted of $\frac{1}{4}$ -in.-OD nickel rods. Exposure conditions and graphical results for Rods 2 and 3 are shown in Figures 20b and 20c. Cumulative exposure was 24 hr at 500 C and 8 hr at 600 C under fluorinating conditions, plus an additional 7 hr at 600 C with no fluorine present. It can be noted that no extreme corrosion has occurred in either Rods 2 or 3 in the vapor phase, although exposures were comparable to those of Specimen 1. Little dimensional change was noted, and there was a maximum intergranular attack of 5 mils at an elevation of 20 in., dropping rapidly to less than 0.5 mil at 30 in. This would suggest some condition during the exposure of Specimen 1 (where high corrosion was observed) that was unique, such as the presence of a minor constituent or of a local metallurgical abnormality. It was noted in Specimen 1 that "grain growth" had occurred in the regions of high attack. Perhaps the large grains were present initially and were responsible for accelerated attack, although one would not expect such acceleration unless grain boundaries were weakened through some other effect.

FIGURE 20a, b, c

VERTICAL CONTOURS OF NICKEL CORROSION SPECIMENS IN FLUID-BED FLUORINATOR

VERTICAL CONTOUR OF NICKEL CORROSION SUPPORT TUBE IN FLUID-BED FLUORINATOR (SPECIMEN 1)

TIME AND TEMPERATURE 20 HOURS AT 500 C
12 HOURS AT 600 C
BED URANIUM-ZIRCONIUM FLUORIDES
FLUIDIZING MEDIUM 15% FLUORINE IN NITROGEN
RUNS U Zr-6B TO U Zr-14
GAS VELOCITY 11 FT/SEC

VERTICAL CONTOUR OF NICKEL CORROSION ROD IN FLUID-BED FLUORINATOR (SPECIMEN 2)

SPECIMEN NO. 2, 1/4-IN. OD ROD
RUNS U Zr-15 TO U Zr-18
TIME AND TEMPERATURE 24 HR AT 500 C
8 HR AT 600 C
7 HR AT 600 C (N₂ ONLY)
FLUIDIZING MEDIUM 15% F₂ IN N₂
BED URANIUM-ZIRCONIUM FLUORIDE
GAS VELOCITY 1.1 FT/SEC

VERTICAL CONTOUR OF NICKEL CORROSION ROD IN FLUID-BED FLUORINATOR (SPECIMEN 3)

SPECIMEN NO 3, 1/4 INCH OD ROD
RUNS U Zr-19 AND U Zr-20
TIME AND TEMPERATURE 16 HR AT 500 C
FLUIDIZING MEDIUM 15% F₂ IN N₂
BED URANIUM-ZIRCONIUM FLUORIDES
GAS VELOCITY 11 FT/SEC

Specimen 4 consisted of two flat strips of nickel (0.032 in. thick x 0.75 in. wide), one for gross corrosion evaluation and the other for analysis of the corrosion film. Exposure time was 32 hr at 600 C. In the region of the specimen ranging from elevation 0 to 32 in., large areas of local attack were evident. The attack consisted of wide shallow pits in areas of otherwise undisturbed metal and were generally located under a tightly adherent film that was difficult to remove. Pit depth averaged about 1.0 to 1.5 mils. No accelerated attack was observed above an elevation of 32 in. No intergranular attack was noted in any of 20 cross sections taken from the strip. This comes unexpectedly relative to previous results. It may be significant that unlike the other specimens, this one had no exposure to the 500 C environment.

b. Comparison of Metals

During Runs UZr-6B to UZr-20, coupons of nickel-base alloys were exposed in the bed. The results of the evaluations are shown in Table 29. Monel appears to be superior in having low rates of dimensional change, and a small amount of intergranular attack. Inconel, although not subject to intergranular attack, is subject to excessive dimensional change. The normally protective film on Hastelloy B appears not to be protective when in contact with a fluid bed, as evidenced by very high rates of dimensional attack.

Table 29

CORROSION OF COUPONS EXPOSED IN FLUID-BED FLUORINATOR

		Location:		In Bed		
		Temperature:		As Noted		
		Fluidizing Gas:		15% F ₂ in N ₂		
		Runs:		UZr-6B to UZr-20		
		Coupon Area:		16.4 sq cm		
Metal	Coupon	Time at 500 C (hr)	Time at 600 C (hr)	Weight Loss (mg) ^a	Dimensional Change (mils/mo) ^b	Intergranular Attack (mils)
"L" Nickel	H12	60	20	324.3	7.9	-
	H2A			343.9	8.4	2.4-3.8
"L" Nickel	H2B ^c	40	8	106.9	4.4	-
	H2C			119.6	4.9	-
Hastelloy B	BO1 ^c	20	12	2495.8	148	Not Evaluated
	BP1			2583.6	153	
Inconel	LR2	60	20	1356.0	35	None -
	LS2			900.9	23	
Monel	MD3	60	20	69.6	1.7	0.4
	ME3			81.8	2.0	

^aAfter defilming in boiling ammonium oxalate.

^bAssuming linear rate of attack.

^cH2B and H2C replaced BO1 and BP1 after first 32 hr of exposure.

c. Analysis of Corrosion Products

In order to gain an insight into what was occurring on the specimens, scrapings were taken from Specimen 2. The specimen consisted of a 0.250-in.-OD nickel rod that had been placed in the fluorinator. The scrapings were submitted for spectrochemical analyses. The results are summarized in Table 30 and reported graphically as a function of elevation in Figure 21a and 21b. It will be noted that nearly all constituents reach a peak concentration in the range of 30 to 45 in. above the gas-distributor plate. The normal bed height is about 12 in. The magnitude of the peaking varies from metal to metal - chromium, copper, and tin having more pronounced peaks, while iron and lead have less pronounced peaks. Referring to the corrosion data for this specimen (Figure 21b), it is noted that there was little dimensional change and maximum intergranular attack of 5 mils at an elevation of 20 in., dropping rapidly to less than 0.5 mil at 30 in. Hence, one can conclude that high corrosion does not accompany any of the peaking observed in Figure 21. Of process interest is the high gradient of the uranium concentration in the top of the unit. This is an indication that some of the hexafluoride is reacting in the upper parts of the column, and proper column design is necessary to minimize this.

Table 30

SUMMARY OF SPECTROCHEMICAL REPORT^a OF SCALE TAKEN FROM NICKEL ROD
CORROSION SPECIMEN 2 FROM FLUID-BED FLUORINATOR

Runs UZr-15 to 18
Time and Temperature 24 hr at 500 C 8 hr at 600 C 7 hr at 600 C (nitrogen only)
Fluidizing Gas 15% F₂ in N₂
Bed Uranium-zirconium-fluoride
Specimen 1/4-in -OD nickel rod

Elevation ^b (in above bottom of bed)	Element (%)														
	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	Ti	U	Y	Zr
1	0.04	0.3	-	-	1	-	0.02	0.2	60	-	-	0.02	-	-	12
15	0.04	0.2			15	0.5	0.03	0.1	30	-	6	-			50
30	0.15	0.4	0.6	0.04	4	0.5	0.07	2.5	40	0.4	20	0.2		0.001	25
32	0.2	0.4	2	0.1	6	0.7	0.05	3	50	0.7	20	0.4		0.001	30
34	0.3	0.2	2	0.15	8	0.5	0.03	4	40	0.8	20	0.6		0.001	40
36	0.3	0.2	2	0.2	5	0.5	0.03	4	40	1	15	0.4		0.004	30
38	0.2	0.4	2	0.2	4	0.5	0.05	4	40	0.8	20	0.4		0.007	50
40	0.2	0.4	1.5	0.1	5	0.8	0.02	3	12	0.6	10	0.1		0.01	60
42	0.2	0.4	3	0.2	5	0.8	0.03	4	20	0.8	15	0.2		0.03	70
44	0.1	0.2	2	0.08	3	0.4	0.04	3	10	0.5	16	0.2	<0.5	0.02	70
46	0.1	0.1	2	0.1	5	0.4	0.02	3	13	0.5	12	0.1	"	0.02	70
48	0.04	0.1	2	0.04	2.5	0.3	0.02	3	13	0.4	16	0.04	"	0.01	60
50	0.04	0.1	1.5	0.02	2	0.1	0.02	3	8	0.5	10	0.06	"	0.01	50
52	0.03	0.1	1.5	0.02	3	0.2	0.02	3	8	0.7	12	0.08	0.5	0.01	50
55	0.05	0.2	1.5	0.07	4	0.4	0.05	2	10	1	12	0.2	2	0.02	50
60		0.05	0.7	0.03	2	<0.1	-	1	6	0.5	10	0.3	30	0.02	50
75	-	0.05	<0.2	0.06	1	<0.1	-	0.15	1	<0.2	<0.5	1.5	70		25

^aAccuracy of data a factor of two

^bBed height about 12 in

FIGURE 21a
SPECTROCHEMICAL ANALYSES OF SCALE FROM
FLUID-BED CORROSION SPECIMEN 2

FIGURE 21b
SPECTROCHEMICAL ANALYSES OF SCALE FROM
FLUID-BED CORROSION SPECIMEN 2

During the course of the fluorination runs, spectrochemical analyses were made of a number of different solids including the final bed, wall scale above bed, wall scale near the bed, scale in product, and product free of scale. An effort was made to correlate these analyses with the corrosion effects observed (up to Run UZr-18). In general, there were few differences observed between 500 C and 600 C runs, and those in which Specimen 1 or Specimen 2 had been in place. It was noted that manganese contents of the final bed, scale in product, and product free of scale ranged from 0.03 to 0.5 percent in runs where Specimen 1 was installed to less than detectable (about 0.01 percent) for Specimen 2 runs. It may be that the presence of manganese accelerates corrosion of nickel in fluorine.

d. Bench-scale Tests

A series of bench-scale tests were made to determine the effects of zirconium tetrafluoride and various additives on the corrosion of nickel and Monel in a fluorine atmosphere. The effect of impurities in the commercial fluorine gas was also investigated. The basic test unit is shown in Figure 22. The inner of the two tubes is the test specimen, and the annular space is filled with zirconium fluoride plus additive. A decreasing temperature gradient was intentionally provided to enable possible volatile materials to escape the bed and condense in higher portions of the equipment. The tubing specimens were annealed, fine-grained "A" nickel, all from the same heat of material.

FIGURE 22
EXPERIMENTAL APPARATUS FOR
DETERMINING EFFECT OF ADDI-
TIVES TO ZIRCONIUM TETRA-
FLUORIDE ON THE CORROSION
OF NICKEL IN FLUORINE

Results show that the addition of lead fluoride accelerates both dimensional change and subsurface corrosion, while manganese fluoride was found to increase intergranular corrosion. Additions of the

fluorides of cobalt, chromium, tin, and titanium had no accelerating effect. Table 31 shows the results of tests comparing nickel and Monel and the effect of fluorine impurities. Commercially available fluorine normally contains 98 percent fluorine with hydrogen fluoride as the major impurity. Trace amounts of silicon tetrafluoride and oxygen bifluoride were found. Removal of some of the impurities, especially hydrogen fluoride, was achieved by passing the fluorine through a bed of porous sodium fluoride.

Table 31

SUMMARY OF STATIC CORROSION EXPERIMENTS IN FIXED BEDS OF
ZIRCONIUM TETRAFLUORIDE IN A FLUORINE ATMOSPHERE

Material	Bed	Exposure Time (hr)	Treated Fluorine ^a	Max Bed Temp (C)	Max Dimensional Change (mils)	Intergranular Attack (mils)	
						Typical	Maximum
Nickel ^b	None	70	Yes	600	0.1	0.4	0.5
Nickel ^b	ZrF ₄	70	No	600	1.5	2.7	5.9
Nickel ^b	ZrF ₄ + 5% AlF ₃	28	No	600	0.1	1.2	1.6
Monel	ZrF ₄	70	No	675	> 62 ^c	0	0
Monel	ZrF ₄	49	Yes	675	> 62 ^c	0	0
Nickel ^b	ZrF ₄	70	No	675	4.4	5.6	5.9
Nickel ^b	ZrF ₄	70	Yes	675	4.0	5.7	7.0
Recrystal- lized Al ₂ O ₃	ZrF ₄	7	No	650	0 ^c	-	-

^aFluorine is treated by passing it through a bed of porous sodium fluoride.

^bNickel was "A" nickel, fine grained and annealed.

^cMetal perforated through wall.

The data at 600 C indicate that the presence of zirconium tetrafluoride accelerates the rate of attack on "A" nickel in fluorine - dimensional change and intergranular attack both show an increase. Additions of aluminum fluoride to the zirconium fluoride had no pronounced effect.

The four runs made at 675 C show that Monel has little usefulness in a fluorinated static bed of zirconium fluoride. Whether the fluorine was treated or untreated, the Monel was perforated badly in the zone of highest temperature. No intergranular attack was noted, even in the areas where perforation occurred. The nickel specimens were well intact following the runs. The maximum dimensional change of 4 mils is greater than that observed in the same experiment at 600 C (1.5 mils); intergranular attack was also somewhat greater. No significant difference

appeared between the two tests in which treated and untreated fluorine were used. This is at variance with 600 C data previously obtained in which fluorine pretreatment reduced intergranular attack.

This series of experiments indicates that under the conditions used, nickel is more useful than Monel, particularly in the laboratory, where the intergranular degradation of nickel is not likely to be objectionable. It has not been established whether this is equally true for a fluid bed; no Monel specimen removed from the fluid-bed fluorinator has shown the degree of perforation observed in the static test. The corrosion rate of nickel in a static bed was not so high as to preclude its use under some conditions.

Two samples of recrystallized alumina were exposed to fluorine at 650 C for 7 hr. No dimensional changes were observed; weight gains were negligible, 0.9 and 2.0 mg/sq cm.

IV. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The successful operation of a fluid-bed dryer equipped with two-fluid spray nozzles for processing aqueous uranium-zirconium-fluoride fuel solutions has been demonstrated. The dried salts, primarily zirconium tetrafluoride, are deposited as a coating on the fluidized particles. Agglomeration of particles occurred only at high feed rates. With the use of an internal autoresistance heater it was possible to operate the dryer at feed rates of 210 ml/min [17 gal/(hr)(sq ft)]. Particle growth may be controlled by the use of air-attrition jets inserted within the fluidized bed. The process was demonstrated in continuous runs up to 54 hr long. This technique of fluid-bed drying has more widespread applicability to other fuel types by choosing the proper dissolving medium and materials of construction.

Uranium removal to the extent of 90 to 95 percent from solids prepared in the fluid-bed dryer has been achieved in a fluid-bed fluorinator. Nearly quantitative uranium separation may be achieved with fluorine at temperatures near 650 C in static-bed equipment. The dryer material from which this degree of recovery has been attained most consistently was produced under conditions such that the major portion of it consisted of zirconium tetrafluoride with a portion of zirconium tetrafluoride monohydrate present. A hydrofluorination pretreatment prior to fluorination removed the water of hydration, thereby increasing the porosity of the particles. Fluorinations at temperatures above 650 C resulted in caking of the dryer products so a disposable fluorinator concept, which would provide the vessel for storage of the active waste after the uranium was removed, has been developed. Nickel appears to be the most suitable material for the fluorination step.

Recommendations

1) The effect of dryer conditions: residence time, hydrogen fluoride concentration in the dryer, and temperature, on the chemical composition of the dryer products should be studied in more detail. Since the quantity of residual oxygen and/or water may influence the extent of uranium removal by fluorination, this information will be necessary in specifying dryer conditions.

2) Before any process specifications can be assigned to the fluid-bed drying operation, further experimental work will be necessary in determining the rate of particle growth in the dryer, and obtaining data on the rate of particle attrition by air jets as a means of controlling particle growth. The continuous successful operation of the fluid-bed dryer depends on precise balance between particle growth and attrition.

3) The basic factors affecting sintering of particles should be investigated especially as regards its effect on uranium removal during fluorination.

4) Determination of whether the reaction of uranium hexafluoride with the bed materials is a deterrent to complete uranium removal.

5) The exact nature of the residual uranium compounds should be determined. This may give rise to a scheme whereby the uranium can be completely separated from the matrix material. Identification of forms such as uranium-zirconium solid solutions may be necessary.

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VI. APPENDIX

A. Disposable Fluorinator Design

Introduction

In several fluoride volatility process schemes applied to the recovery of uranium from spent fuel elements, a substantial quantity of highly radioactive nonvolatile material remains as residue from the final fluorination. A disposable fluorinator used in this step has the advantage of eliminating a final material transfer to a separate waste container for disposal. The requirements for such a vessel are 1) ability to withstand process conditions for single-batch operation, and 2) ability to retain integrity as a primary waste container. The chief problem in the design of such a vessel is to keep the cost sufficiently low so that the overall batch cost is not increased substantially. The design must also be suitable for remote coupling and uncoupling.

A specific design was developed for the final fluorination step in the ADF process for recovery of enriched uranium from high zirconium-uranium alloys. The major process steps in this scheme are: 1) hydrofluorination of the alloy (aqueous dissolution followed by fluid-bed spray drying, or anhydrous hydrofluorination), and 2) removal of uranium by fluorination up to 700 C. It is probable that an intermediate step may be advantageous to remove hydrogen and/or oxygen from the initially hydrofluorinated material. If fluorine is used, some uranium will also be removed in this step. Experiments to date indicate that removal of the last traces of uranium by fluorination requires temperatures up to 700 C. At this temperature the zirconium fluoride bulk material sinters and is no longer mobile. The advantage of a disposable fluorinator for the final fluorination is evident.

Other uses of a disposable fluorinator are possible:

1. for carrying out all or several process steps of the zirconium-uranium recovery process,
2. for carrying out fluorinations in fused fluoride processes,
3. for disposal and packaging of radioactive solids in other processes which may consist of highly toxic radioactive dusts.

Corrosion Aspects

In experimental tests on the ADF process, hundreds of hours of processing have been carried out in 3-in., Schedule 40 pipe reactors of both nickel and Monel with no failures. General experience has been that nickel is preferable to all other metals for high-temperature fluorinations.

Quantitative corrosion data have been obtained from coupons exposed in pilot-plant runs and in separate bench-scale corrosion tests. The most consistent results at 600 to 700 C in the typical environment show dimensional attack and intergranular attack each of the order of 1 to 5 mils in exposure periods of 15 to 70 hr. One test (see Fig. 20, page 76) showed dimensional attack as high as 47 mils in a pilot-plant exposure of 20 hr at 500 C and 12 hr at 600 C. This high value could not be reproduced, and it was concluded that a very special uncontrolled variable had been involved, possibly the metallurgical state of the metal coupon itself.

For design purposes, it has been considered here that the processing step would involve a maximum fluorination time of 10 hr and a maximum temperature of 700 C. For this, a maximum corrosion of 5 mils dimensional attack and 5 mils intergranular attack would be expected. A corrosion allowance of 15 mils is considered realistic for design.

Size of Batch

Both process feasibility and economic attractiveness enter into the selection of batch size. Economics favors larger batches against which to charge the disposable vessel cost. From other standpoints, however, the larger size involves somewhat more difficulty. One of these is the greater handling problem. The range of practical size is considered to be a vessel diameter of 1 to 2 ft and a vessel height of 4 to 8 ft. The detailed design considered here was made for the largest size in this range, namely, 2-ft diameter and 8 ft tall. For this size of vessel the processing batch is of the order of 2500 lb total; and for a feed material with uranium concentration of 1 w/o, about 12 kg of enriched uranium is initially contained in the batch.

Basic Vessel Design

The basic design of the vessel has the following features:

1. the vessel is a closed, thin-wall container of nickel;
2. inlet and outlet process lines are located at the top, the connection being flanged with copper gaskets used only once;
3. the vessel is transported and supported from a bracket at the top.

A sketch of the vessel is shown in Figure 23. The vessel is cylindrical with standard ASME dished heads to give good strength with a minimum amount of material required. Inconel support arms are used for strength at high temperature. A single flange is used for both processing lines and this enables both lines to be sealed in one operation.

The flange sealing or clamping device is shown in Figure 24. A clamp holds the upper permanent flange located at the mounting position and the vessel flange by means of a pair of retractable wedge-bars that move in under the vessel flange. A worm gear arrangement is used to move the wedge clamp bars. A 5° taper on the wedge together with the mechanical advantage of the worm gear gives an overall mechanical advantage of approximately 1000. Thus, 20 lb applied on a 20-in. hand wheel can apply 20,000 lb of total force for the flange seal, neglecting friction. This is in excess of that required for the gasket loading.

FIGURE 24
LAYOUT OF PROPOSED FLANGE SEALING DEVICE
FOR DISPOSABLE FLUORINATOR

Remote Operation Facility

The remote handling facility consists of a fixed processing flange connection to the vessel, a movable furnace, and a carriage support to move the vessel in and out of position under the processing flange. An overhead crane is used to move the vessel in and out of the processing cell. Limited visual operation is assumed for crane manipulation and checking the remote seal function.

The operations are described below in detail in terms of the four positions shown in Figure 25. In Position A the vessel is shown resting in the cell conveyor, the furnace head is shown empty, and the furnace is shown in its lowered and retracted position.

Step 1 - The empty vessel is lowered onto the conveyor carriage in the shielded cell. The removable shielding block may be replaced after this step (Position A).

Step 2 - The conveyor moves the vessel on its track horizontally to the point where the vessel support bracket engages the elevating arms at the furnace head. This point may be detected visually or by feel of the conveyor. As the conveyor continues to move further in the same direction, the vessel would be picked off the conveyor support and held solely on the elevating arm. In this case the vessel would drop the small fraction of an inch that makes up the clearance between the elevating arms and the carriage support. This drop could be eliminated, however, by stopping the carriage when the vessel is in position over the elevating arm support and then raising the vessel off the carriage support by moving the elevating arm upward. In either case the vessel is raised vertically by the elevating arm until the vessel flange makes contact with the fixed flange at the processing head (Position B).

Step 3 - Elevating arms* raise the vessel to make flange connection and the flanges are clamped to make the gaskets seal (Position C). Some force for the flanged connection is applied by the elevating arms. However, the upward force supplied by the elevating arms is limited by a strain gage indicator at the fixed flange position. The processing lines are sufficiently flexible for the slight movement involved. The major force for the gasket seal is provided by the wedge clamp device which is actuated as shown by an extension handle and can be operated manually from outside the shielded cell.

*A pair of worm-gear jacks, motor driven, are used to raise the elevating arms. The grip part of the arm which holds the vessel incorporates a locking device to prevent the vessel from accidentally slipping off the arms. This locking device is tripped when transfer to the conveyor is required.

FIGURE 25a
SCHEMATIC DIAGRAM OF FLUORINATION CELL - POSITION "A"

FIGURE 25b
SCHEMATIC DIAGRAM OF FLUORINATION CELL - POSITION "B"

FIGURE 25c

SCHEMATIC DIAGRAM OF FLUORINATION CELL - POSITION "C"

FIGURE 25d

SCHEMATIC DIAGRAM OF FLUORINATION CELL - POSITION "D"

Step 4 - Two lines extend from the top of the vessel in a common rectangular flange. One of these, a 2-in. line, is an upline used for charging powder to the vessel initially and later for uranium hexafluoride off-gas. The other line, 1-in. tubing, is a downline extending to a few inches of the bottom and is used to introduce the fluorine. The two openings in the rectangular flange are closed with individual copper ring gaskets which have been cemented in position before introduction into the cell.

Step 5 - The furnace is raised around the vessel and contact made with the furnace head (Position B). A hydraulic lift is shown for safety reasons installed underneath in the floor. The outer shell of the furnace body provides a secondary seal around the process vessel. It is not considered necessary that this be an absolute seal, but one sufficient to allow a slight negative pressure inside the furnace, so that any leaking material could be exhausted from a furnace vent system provided with its own caustic scrubber and filter. The temperature at the outside of the furnace liner where the seal is affected is sufficiently cool so that Teflon or other elastomers may be used for a gasket seal. The electrical leads to the furnace are required to be flexible to allow for the indicated motion.

Step 6 - After a preliminary leak test, inert fluoride lump material, such as calcium fluoride, is introduced to the vessel to serve as a gas distributor. The vessel is then loaded with a solid powder charge of approximately 2500 lb. The hopper can be weighed and solids discharged from the hopper by a screw feeder. A double valve system with intermediate purge space for both the solid addition and the UF_6 off-gas is shown.

Step 7 - Fluorination is carried out up to 700 C. In order to speed heating, the powder charge may be preheated to possibly 400 or 500 C.

Step 8 - After conclusion of the fluorination, the vessel is purged with nitrogen and the furnace is lowered for cooling (Position C).

Step 9 - Process valves are closed and the flange unclamped. The elevating arms now lower the vessel (Position B).

Step 10 - The conveyor now moves back along the rail to pick up the vessel. As previously, the conveyor may be stopped in position and the vessel lowered onto the conveyor or the vessel may be picked up in a continuous motion with the vessel dropping a small fraction of an inch that makes up the clearance between the elevating arms and the conveyor. The clearance in this case is of course the reverse of the pickup step.

Step 11 - In the position free of the processing head, cone-shaped plugs are inserted in the open vessel lines and driven and brazed into place. This entails a remote manipulator operation.

Step 12 - The vessel is now brought out of the processing cell with the crane and placed in a shielded coffin for transport to a waste-disposal location for storage or burial.

Stress Specifications

Since the largest part of vessel cost is that of the material, the thickness of metal stock should be a minimum consistent with maintaining vessel integrity under processing conditions. Because of the costly and reactive nature of the process materials, well-established design specifications should be followed - those of the ASME unfired pressure vessel code. The code standards should apply to normal, long-term operation; for very short-term emergency operation, safety factors lower than the code requires would be realistically adequate, especially in the region where long-term creep is limiting in the code.

The strength of nickel drops off strongly with temperature. Variations in strength can be seen from values presented in Table 32 for room temperature and 700 C (1300 F). Analysis of design under typical process conditions is presented below in terms of safety factors. These safety factors for both given tensile strength and allowable by the ASME code are considered. A summary of these results are given in Table 33. As shown in the table, the effective cross-sectional area of the metal is reduced to 88 percent and 76 percent of the two reference values by the 15-mil allowance for corrosion. The net safety factors are obtained by multiplying the given safety factors by these percentages.

Table 32

STRESS SPECIFICATIONS FOR NICKEL^a

	Temperature Conditions	
	Room	700 C
Yield strength, psi (0.2% offset)	~20,000	9000
Allowable stress, psi (ASME Code)	7,500	1200
Creep strength, psi ($\frac{1}{10}$ % creep in 10^4 hr)	~20,000	900
Creep strength, psi (1% creep in 10^3 hr)	~20,000	2400 (600 C)

^aInternational Nickel Company Bulletin T-13.

Table 33

SPECIFICATIONS FOR DISPOSABLE FLUORINATOR

Vessel: 2-ft diameter x 8 ft high,
welded nickel sheet, dished heads
Process temp: 700 C

	$\frac{1}{8}$ -in. Wall	$\frac{1}{16}$ -in. Wall
Stress on circumferential section under charge weight (2500 lb), psi	260	520
Safety Factor, yield point	34	17
Safety Factor, ASME Code	4.5	2.2
Stress on circumferential section under 10 psi internal pressure, psi	480	960
Safety Factor, yield point	19	9.5
Safety Factor, ASME Code	2.5	1.2
Stress on longitudinal section under 10 psi internal pressure, psi	740	1480
Safety Factor, yield point	13	6.5
Safety Factor, ASME Code	1.6	0.8
Wall section after 15-mil corrosion allowance, % of original thickness	88	76

From data in Table 33, it appears that the $\frac{1}{8}$ -in. wall will meet code specifications for pressures to 10 psi at 700 C, but that the $\frac{1}{16}$ -in. wall will not.

Cost Estimate of Materials

Retail prices of low carbon nickel and Inconel sheet are taken as \$1.50 per pound, figures conservatively based on price data in January 1959. Seamless low-carbon nickel tubing is taken at \$2.00 per lb. The cost of forming the 24-in.-diameter head is taken at \$6.80 each, based on Lukens catalog prices. An additional \$2.50 is allowed for machining and bevelling the head flange. The cost of head forming thus totals \$18.60 per vessel. The material cost for the vessel is itemized in Table 34, and totals \$715 for a vessel with $\frac{1}{8}$ -in.-thick walls and a $\frac{3}{16}$ -in.-thick head. If a $\frac{1}{16}$ -in.-wall vessel with a $\frac{1}{8}$ -in. head could be used, the material cost would be nearly halved, that is, \$420.

Table 34

MATERIAL COST FOR DISPOSABLE FLUORINATOR
VESSEL

Cylindrical vessel: 2-ft diameter x 8 ft high;
dished heads.

Material: Low carbon nickel except as noted.

Vessel Body Material	\$414.00
48 sq ft of $\frac{1}{8}$ -in. sheet	
Vessel Head Material	211.00
two 30-in. circles, $\frac{3}{16}$ -in. sheet	
Head-forming Charge	19.00
Vessel Process Connections	31.00
$\frac{3}{32}$ -in. wall, nickel tubing	
Vessel Process Flange, Monel	5.00
3 x 6 x 1 in. overall	
Inconel Support Arms	30.00
Steel Channel	5.00
	<hr/>
Total Material Cost	\$715.00

Cost Estimate of Fabrication

Economical manufacture of course depends on highly efficient quantity production. It is assumed that orders for several hundred vessels would be processed at once. Welding of the sheet is assumed to consist of one circumferential weld and one full-length longitudinal weld. After the sheet is rolled, two additional girth welds are required to attach the heads,* for a total of about 300 in. of weld. The upper head must be drilled for the tubing, and the tubing cut and welded in place. The rectangular flange must be cut and welded in place. The support arms also are welded. These details are shown from the vessel assembly drawing (see Figure 26). The total estimate of these operations in a production line, exclusive of set-up and jigging, is \$75 per vessel. If \$5000 is allowed for engineering, set-up, and jigging 500 units, this would amount to an additional \$10 per unit. The total fabrication-assembly cost is thus estimated at \$85 per vessel.

Estimated Total Cost and Unit Processing Charge

The sum of the above material and assembly costs is estimated at \$900 for the standard ($\frac{1}{8}$ -in. thick) vessel and about \$600 for the light ($\frac{1}{16}$ -in. thick) vessel.

*For butt welds of sheets of this thickness, the code does not require bevelling. Heliarc welding is called for.

FIGURE 26
ASSEMBLY DRAWING OF DISPOSABLE FLUORINATOR

If, then, \$100 per vessel is added for overhead and profit, the total cost is \$1000 for the standard vessel and \$700 for the light vessel. Since this size of vessel could process over 10 kg of uranium in typical process concentrations, the unit processing cost for the disposable vessel would be about 10 cents/g uranium processed.

Fabrication Specifications

The vessel use does not require close tolerances on overall dimensions, either of the diameter or of the length. This is so chiefly because of top suspension, which leaves the bottom free. Diameter tolerances are involved for fabrication operation in alignment for welding heads. The heads themselves are dished to better than 1 percent out of round; the machined heads should be substantially better than this. Final alignment of the rolled cylinder could be accomplished with a mandrel.

Operations of remote coupling require the vessel to hang fairly evenly from the support arms, that is, within about 1 in. over the full length. The flange position is most critical; it should be centered within $\pm \frac{1}{8}$ in. relative to the support arms.

Leak tightness at 10 psig internal gas pressure is required to the following degrees:

- a) no greater than 10 std - cc/hr,
- b) no greater than 0.01 mm Hg pressure drop/hr,
- c) no more than 3 bubbles/min (under water with 10 psi differential pressure).

It is considered that common leak testing methods are usable:

- a) freon or helium leak detector,
- b) static pressure drop,
- c) water tank test.

Vessel Fabrication and Cost

Details of vessel fabrication and the cost estimate are made on the basis of the minimum thickness of material for one-shot process operation, the vessel to be fabricated in quantity from 100 to 1000 units.

The body of the vessel is made by welding and rolling nickel sheet. Simple butt welds are used. The heads are spun according to ASME standard dimensions, the flange edges machined with a bevel.

Remote Operation

The reference design of the remote-handling device was made with the objective of optimizing ruggedness, simplicity, noncritical alignment, and trouble-free operation in a radioactive field. Where movement is required, unidirectional rather than multidirectional positioning was specified. Primary force transfer linkages were made mechanical, although operation need not necessarily be manual. Torque-limiting devices, microswitch positioners, and strain gages can be used to facilitate operations.

Criticality Considerations in the Disposable Fluorinator

Limited moderation appears to be the only practical way to assure nuclear safety in a disposable fluorination vessel of economically attractive batch size. Dimensionally safe 5-in.-diameter pipe or mass-safe 370-g batches would increase the cost of the fluorination excessively. The use of poisons does not appear promising because:

1. The fluorination step is a weakly moderated or epithermal system in which the poisons (boron or cadmium) are not as effective as in completely thermalized systems.
2. The effect of the poison must be experimentally established, which may be difficult in a system where it is possible to concentrate uranium and hydrogen within the unit without concentrating the poison.
3. Present practice is to use poisons to provide additional safety and not for the purpose of handling larger quantities or concentrations of nuclear materials.

Nuclearly safe batch size as a function of hydrogen concentration for the fluorinator feed material is given in Table 35. The nuclear safe mass is not the critical mass and is subcritical by a sufficient amount to allow for storage and movement of multiple units in the same area under prescribed conditions. The hydrogen content of the fluid-bed dryer products ranges from 0.1 to 1.0 weight percent, which is not low enough to allow economical batch sizes for the fluorination step. Higher temperature operation of the drying or hydrofluorination step may reduce the hydrogen concentration. Also, a separate dry air purge at a high temperature may be necessary if the previous operations cannot achieve a low hydrogen content. It would be necessary to establish the hydrogen concentration of the fluorinator feed before charging to equipment that was not dimensionally safe. Nuclear safety would be most easily assured by a process step which gave consistently safe hydrogen concentrations. If nuclear safety were dependent entirely on analytical results, previous practice would indicate that duplicate samples of each batch would be required to agree within five percent and would need to be safe by a factor of ten.

Table 35

NUCLEARLY SAFE BATCH SIZE AS A FUNCTION OF
HYDROGEN CONTENT

Basis: 100 percent enriched 2 w/o U-98 w/o Zr alloy as ZrF_4 and UF_4 .

Bulk density: 2.0 g/cc.

Hydrogen Content (w/o)	Weight U^{235} (kg)	Total Weight (kg)	Total Volume (cu ft)
1.0	0.54	50	0.88
0.5	0.69	64	1.13
0.2	1.4	131	2.32
0.1	2.5	234	4.42
0.05	4.9	460	8.7
0.02	12	1120	19.8
0.01	19	1770	31.3
0.001	38	3540	62.6

In the fluorination step, uranium is known to concentrate in the downstream part of the bed prior to complete fluorination. It is not known, however, whether moisture or hydrogen fluoride present in the bed would concentrate also, or whether the concentration of the materials would take place at the same time and position.

The dryer product has a uranium density of about 20 g/l. The nuclearly safe mass (Table 35) is based on a density of approximately 100 times this value. Concentration effects during fluorination of this magnitude would not be expected. Since low uranium concentrations tend to reduce neutron multiplication factors, a more realistic evaluation was based on actual process values. The basis was a 2 x 8-ft fluorinator which would contain up to 15 kg of uranium (22 g U^{235} /l) and from 2 to 6 kg of hydrogen. Allowing for a uranium concentration increase to 87 g/l, a multigroup computer program was utilized to determine the allowable hydrogen concentration in the fluorinator. The result indicated that the allowable hydrogen concentration in the dilute system is only slightly larger than determined on the basis of a nuclearly safe mass (409 g versus 185 g hydrogen). This value is still considerably below the hydrogen concentrations in the dryer product, which indicates a need for incorporating a technique of reducing the hydrogen content of the dryer product if a disposable fluorinator of economical size is to be realized.

B. Preliminary Chemical Flowsheet

A preliminary chemical flowsheet (see Figure 27) has been outlined for the ADF Process as based on a design capacity of 1100 kg of uranium

(93 percent enriched) annually. The uranium form would be 2 weight percent uranium-Zircaloy-2 fuel alloy.

FIGURE 27

CHEMICAL FLOWSHEET FOR ADF PROCESS FOR RECOVERY OF
URANIUM FROM URANIUM-ZIRCALOY-2
REACTOR FUEL ALLOYS

[Basis - 100 kg Uranium (93% enriched) Annually -
2 w/o Uranium-Zircaloy-2]

The major process steps include continuous aqueous dissolution of the fuel, fluid-bed drying of the fuel solution, and fluid-bed fluorination of the dryer product to yield the volatile uranium hexafluoride. Final purification of the uranium hexafluoride may be achieved by a fractional distillation step or alternate adsorption-desorption using a sodium fluoride bed.

The flowsheet has been made as simple as possible by having several of the streams recycled. A continuous dissolver is suggested, and the aqueous solution used for dissolution will be the condensate from the fluid-bed dryer off-gas stream. Enough anhydrous hydrofluoric acid will be added as part of the fluidizing gas in the dryer to give the condensate the proper fluoride concentration, about 7.8 M.

Since it is necessary to add an oxidizing agent such as nitric acid, hydrogen peroxide (or other) to solubilize the tin and to oxidize the uranium to the hexavalent (soluble) state, it will be necessary to add a small side-stream of oxidant to the recycling condensate to replace that which has been used up or destroyed during the dissolution and fluid-bed calcination steps.

It is assumed that the nitrate, which is decomposed in the dryer, will be recovered in the condensate; however, additional nitric acid for dissolution of tin and oxidation of uranium in the alloy will be added as a small sidestream to make the solution about 1.0 M nitrate. The hydrogen from the dissolver will be burned.

The feed solution to the dryer will be about 1.65 M in zirconium and have a fluoride-to-zirconium mole ratio of 4.5. Multiple spray nozzles and probably two or more dryers will be required depending on the criticality aspects of the process. A feed rate of 51.5 liters/hour will be required to maintain the design capacity. The noncondensable off-gas from the dryer, consisting of the combined fluidizing, atomizing, blowback, purge, and fission product gases, will be recycled for fluidizing the dryer bed except for the excess which will be bled to the waste gas system, which includes sodium fluoride traps, a caustic scrubber and the stack. The dryer output will be about 15 kg/hr of granular solids and will contain about 97 weight percent zirconium fluoride, about 1.4 weight percent uranyl fluoride, and the remainder will be minor constituent fluorides.

The fluid-bed fluorination will probably be a batch operation because of the time required for complete removal of the uranium. The fluorine will be recycled for economic reasons, and any excess gas, such as oxygen from the uranyl fluoride, will be bled to the waste-gas processing system. Some fluorine will be lost in this operation. The average production rate of uranium hexafluoride will be about 230 g/hr. This material will require a final purification step.

The waste products will consist mainly of about 340 kg/day or 5.75 cu ft/day of dry, radioactive solids from the fluorinator and additional material from the sodium fluoride traps which will contain adsorbed fission products. In addition, the caustic from the scrub tower will require occasional processing.

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