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**ENGINEERING DEVELOPMENT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES**

**Part 12. Exploratory Tests on Fluorination
of Uranium Oxide with BrF_5 in a
Bench-scale Fluid-bed Reactor System**

by

J. D. Gabor and D. Ramaswami

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Chemical Engineering Division

August 1967

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ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

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ABSTRACT

Through the use of BrF_5 , uranium and plutonium can be separated in a single fluorination step. BrF_5 selectively fluorinates uranium from UO_2 fuels as the volatile UF_6 while converting plutonium oxide to nonvolatile PuF_4 .

A series of 21 exploratory runs on the development of a BrF_5 fluorination process was conducted with a $1\frac{1}{2}$ -in.-diam fluid-bed reactor. These runs were made with UO_2 pellets (no plutonium). For each run, except for the tests to determine the feasibility of direct fluorination of UO_2 , the UO_2 pellets were pulverized to U_3O_8 by oxidation before being fluorinated with BrF_5 . The conclusions were:

1. The lowest fluorination temperature with BrF_5 for practical operation is 200°C .
2. The rate of fluorination increases with the concentration of BrF_5 in the range of 10 to 50 v/o BrF_5 in nitrogen.
3. Direct fluorination of UO_2 pellets with a mixture of 10 to 20 v/o BrF_5 and 30 v/o oxygen in nitrogen at 300 to 400°C essentially does not proceed.
4. A small concentration of BrF_5 (1 to 2 v/o) acts as a promoter for fluorination of U_3O_8 with elemental fluorine at low temperatures ($\sim 200^\circ\text{C}$).
5. A 3-hr run, consisting of alternate oxidations and fluorinations, resulted in a slight increase in oxidation of UO_2 to U_3O_8 fines and a slight decrease in the fluorination of the U_3O_8 to UF_6 in comparison to another 3-hr run consisting of 1 hr oxidation followed by 2 hr of fluorination.
6. The fluorination with BrF_5 proceeds smoothly in a fluid-bed reactor. No bed caking was observed in any of the runs.

I. INTRODUCTION

The use of BrF_5 as a fluorinating agent is presently being considered for the fluid-bed fluoride volatility process for low enriched UO_2 fuels containing plutonium. Jarry and Stockbar¹ found that BrF_5 selectively fluorinated uranium from UO_2 fuels as the volatile UF_6 while converting plutonium oxide to nonvolatile PuF_4 . Thus, through the use of BrF_5 , uranium and plutonium can be separated in a single fluorination step. The plutonium can be recovered in a subsequent step by fluorination of the PuF_4 with elemental fluorine.

Exploratory tests with a $1\frac{1}{2}$ -in.-diam fluid-bed reactor have been conducted for development of a BrF_5 process. These experiments were made with UO_2 pellets (no plutonium). For each experiment, except for the tests to determine the feasibility of direct fluorination of UO_2 , the UO_2 pellets were pulverized to U_3O_8 by oxidation before being fluorinated with BrF_5 . Experiments were also performed with mixtures of fluorine and BrF_5 to explore possible alternative schemes for conducting the fluorination step.

The objectives of these bench-scale tests were:

1. To establish the optimum temperature for BrF_5 fluorination.
2. To determine the effect of BrF_5 concentration on the rate of fluorination.
3. To determine if it is feasible to directly fluorinate UO_2 with BrF_5 without previously oxidizing the UO_2 to U_3O_8 .
4. To determine if BrF_5 has a promotional effect on fluorination with elemental fluorine.
5. To demonstrate the operability of a fluid-bed reactor for this process (bed caking was the prime concern).

II. EQUIPMENT AND PROCEDURE

The equipment for these tests was previously used for studies on the fluid-bed fluoride volatility process for the recovery of uranium from enriched uranium-zirconium alloy fuels.² Figure 1 is a schematic diagram of the reactor system.

The fluid-bed reactor was constructed of nickel-200. The reactor consisted of three sections joined by flanges: (1) the gas distributor, made up of an inverted 60°C cone with a single $1\frac{1}{4}$ -in. IPS connection at the apex for feeding gases and draining beds; (2) the fluid-bed section, a 14-in. length of 1.5-in. IPS pipe; and (3) the disengaging section, a 14-in. length of 3.0-in. IPS pipe, with its lower end necked down to mate with the fluid-bed section.

308-253

Fig. 1. Schematic Diagram of Reactor System for Exploratory Studies of BrF_5 Fluorination

stillpot weight changes. The off-gas from the reactor was filtered by a packed bed of -14 +28 mesh alumina. The filter bed was contained in a vessel fed by the off-gas line from the reactor and was maintained at the same temperature as the reactor bed. In several of the later runs, the packed-bed filter was replaced by two nickel bayonet filters* (9 in. long by $1\frac{1}{4}$ in. wide, G porosity) installed in the disengaging section of the fluid-bed reactor. Filter blowback, either manual or automatic, was accomplished by high-pressure nitrogen through venturis.

Four soda lime traps, each 4 in. OD by 24 in. high, with a total soda lime capacity of 12 kg, disposed of the off-gas. The traps were constructed of $1/8$ -in.-thick copper tubing with $1/4$ -in.-thick copper flanges. Two traps operated in series. One trap served as a secondary trap, and the other three served as primary traps. The initial temperature of the soda lime was 100°C . Since the reaction of BrF_5 with soda lime is exothermic, and since UF_6 will desorb from NaF (a reaction product from BrF_5 and soda lime) at 400°C , the gas flow was switched to an alternate trap when the trap skin temperature reached 200°C .

Face shields, leather jackets, and leather gloves were worn by personnel during transfers of BrF_5 from the manufacturer's cylinder to the stillpot. Calcium fluoride powder was stored for absorbing interhalogens in case of a spill. Carbon dioxide fire extinguishers were also available to stop small leaks temporarily by freezing and for use in case of fire.

For each run, 270 g of UO_2 pellets and 470 g of nominal 48 to 100 mesh alumina** were charged to the reactor; 100 g of -14 +28 mesh alumina in the cone section at the bottom of the reactor served as a support

The BrF_5 was supplied from a cylindrical stillpot 6 in. in diameter by 8 in. high (213 cu. in. in volume). The stillpot was fabricated from Schedule 40 6-in. nickel pipe and nickel plate, $1/4$ in. thick, welded at the top and bottom. The vessel was heated electrically, and an automatic shutoff and alarm combination prevented excessive pressure buildup or temperature rises.

The BrF_5 flow rate was measured by a thermal flow-meter, a Kel-F rotameter, and

*Pall Trinity Micro Corporation, Glen Cove, New York.

**Type T-61, Tabular Alumina, manufactured by Aluminum Company of America.

for the UO_2 pellets and as a fluidizing-gas distributor. Periodically, samples were taken from the fluid bed. When a packed-bed filter was used, 100 g of -14 +28 mesh alumina was charged to it.

All tests (except tests on the direct fluorination of UO_2) were conducted in two steps: (1) oxidation of UO_2 pellets to U_3O_8 fines, followed by (2) fluorination of the U_3O_8 to UF_6 .

III. RESULTS AND DISCUSSION

There were four major areas of exploratory investigation:

1. The determination of the effect of temperature on the fluorination rate.
2. The determination of the effect of BrF_5 concentration on the fluorination rate.
3. The determination of the feasibility of directly fluorinating UO_2 with BrF_5 .
4. The determination of possible promotional effects of small concentrations of BrF_5 on fluorination with elemental fluorine.

A run was also made to see if the addition of a small amount of fluorine gas to the BrF_5 reagent gas had a beneficial effect on the fluorination. Twenty-one runs were made in all.

A. Effect of Temperature

Five runs (BrR-1 to BrR-4 and BrR-7) were made at fluorination temperatures of 385, 290, 200, 175, and 110°C to determine the minimum temperature for practical operation. Before fluorination, the UO_2 pellets were oxidized to form U_3O_8 fines at approximately 400°C with 30 v/o oxygen in nitrogen. Run conditions are given in Table I. The BrF_5 concentration

TABLE I. Run Conditions for Determination of the Effect of Temperature on Fluorination with BrF_5

Column diameter:	1.5 in.				
Bed charge:	270 g of UO_2 pellets (0.5-in. diameter by 0.5 in. long) 470 g of nominal 48 to 100 mesh alumina				
Pellet-bed depth:	1 in.				
Fluid-bed depth:	7 in. (static height)				
Diluent gas:	Nitrogen				
	BrR-1	BrR-2	BrR-3	BrR-4	BrR-7
Oxidation					
Time, hr	3	3	3	3	3
Superficial gas velocity, ft/sec ^a	0.64	0.46	0.5	0.5	0.5
Oxygen concentration, v/o	28.2	33.4	30	30	30
Temperature, °C	440	415	400	385	400
Fluorination					
Time, hr	2.17	2.5	2.5	2.5	0.5
Superficial gas velocity, ft/sec ^a	0.70	0.55	0.5	0.5	0.5
BrF_5 concentration, v/o	7.5	9.2	13.8	11.9	49.0
Temperature, °C	385	290	200	110	175
Total BrF_5 feed, g	430	610	1135	1405	960

^aAt operating temperatures and 1 atm pressure.

in nitrogen diluent for Runs BrR-1 through BrR-4 varied from 7.5 to 13.8 v/o. In Run BrR-7, the BrF_5 concentration was increased to 49.0 v/o to compensate for the low temperature (175°C).

The uranium concentrations in the fluidized alumina during the fluorination for Runs BrR-1 to BrR-4 are plotted in Fig. 2. Each point is based on an analysis of samples withdrawn from the bed through the

Fig. 2. Uranium Concentration in Fluid-bed Alumina during Fluorination with Bromine Pentafluoride

because of deposits (probably resulting from hydrolysis of UF₆ by the high moisture releases from the soda lime) in the Hoke diaphragm valves in the soda lime trapping system. During this high pressure drop, feed rates were depressed, and a reduction in reaction rate was indicated by bed samples taken after 1 hr (1.6 w/o uranium) and 1.5 hr (1.4 w/o uranium). The run was resumed after cleaning of the valves and lines, and uranium was removed down to 4.7×10^{-3} w/o in the final bed.

After Run BrR-7 (175°C and 49 v/o BrF₅), the reactor bed contained 4.62 w/o uranium. The packed-bed filter collected 35 g of uranium fines.

The data from these five runs indicate that the lowest temperature at which practical fluorination rates are achieved is about 200°C; the final bed at 200°C contained 0.17 w/o U.

The UF₆ production rates were calculated for the first four runs on the basis of the uranium in the alumina-bed samples. The results of the

1/4-in. sample line, except for the final point, which represents an analysis of the fluidized bed after it was drained from the reactor. The initial uranium concentration, based on the weight of material charged, should have been 31.7 w/o (37.4 w/o U₃O₈) for each of the four runs. However, because of a possible combination of (1) elutriation losses from the fluid bed to the packed-bed filter, (2) poor bed mixing in the lower portion of the reactor because of high fines concentration, and (3) incomplete pulverization of the UO₂ pellets, the initial concentrations in the bed samples ranged from 10 to 48.7 w/o uranium. The final concentrations of uranium in the bed after fluorination decreased from 10.3 w/o to 2.7×10^{-3} w/o as the reaction temperature was increased from 110 to 385°C.

During Run BrR-2 (290°C), the fluorination was interrupted because a high pressure drop developed across the soda lime disposal system after 90 min of operation. This high pressure drop occurred

calculations (Figs. 3-6) show that during the first half-hour, the production rates exceeded 100 lb UF_6 /(hr)(sq ft) for the runs at 200°C or greater. For the run at 110°C, the initial production rate was 59 lb UF_6 /(hr)(sq ft).

Fig. 3. Uranium Hexafluoride Production Rates during Fluorination with Bromine Pentafluoride for Run BrR-1

Fig. 4. Uranium Hexafluoride Production Rates during Fluorination with Bromine Pentafluoride for Run BrR-2

Fig. 5. Uranium Hexafluoride Production Rates during Fluorination with Bromine Pentafluoride for Run BrR-3

Fig. 6. Uranium Hexafluoride Production Rates during Fluorination with Bromine Pentafluoride for Run BrR-4

On the basis of BrF_5 being reduced to BrF_3 , the fluorination efficiency for BrR-1 was about 115%, indicating that BrF_5 was reduced beyond BrF_3 . The fluorination efficiency based on the total fluorine content of the BrF_5 fed during Run BrR-1 was 46%.

The bed temperatures for each run were maintained at approximately the desired temperature throughout the entire fluorination step with no temperature excursions occurring. No bed caking occurred, and the alumina bed was free flowing after each run.

B. Effect of BrF_5 Concentration

Two subsequent Runs (BrR-5 and BrR-6) were made to determine the effect of BrF_5 concentration on the rate of fluorination of U_3O_8 . These runs also consisted of an oxidation step followed by the fluorination step. The fluorination steps were conducted at 205°C with 29.4 v/o BrF_5 , and at 230°C with 40.5 v/o BrF_5 (see Table II for operating conditions).

TABLE II. Run Conditions for Determination of the Effect of BrF_5 Concentration on Fluorination Rate

Column diameter:	1.5 in.		
Bed charge:	270 g of UO_2 pellets (0.5-in. diameter by 0.5 in. long) 470 g of nominal 48 to 100 mesh alumina		
Pellet-bed depth:	1 in.		
Fluid-bed depth:	7 in. (static height)		
Diluent gas:	Nitrogen		
	BrR-3	BrR-5	BrR-6
<u>Oxidation</u>			
Time, hr	3	3	3
Superficial gas velocity, ft/sec ^a	0.5	0.5	0.5
Oxygen concentration, v/o	30	30	30
Temperature, °C	400	410	400
<u>Fluorination</u>			
Time, hr	2.5	0.83	0.58
Superficial gas velocity, ft/sec ^a	0.5	0.5	0.5
BrF_5 concentration, v/o	13.8	29.4	40.5
Temperature, °C	200	205	230
Total BrF_5 feed, g	1135	850	700

^aAt operating temperature and 1 atm pressure.

The concentration of uranium in the bed after 0.83 hr of fluorination with 29.4 v/o BrF_5 was 1.54 w/o, and the filter bed contained 9 g of uranium

fines. The uranium concentration was 0.29 w/o after 0.58 hr of fluorination with 40.5 v/o BrF_5 , and the filter bed had gained 17 g in weight. In Run BrR-3 with 13.8 v/o BrF_5 at 200°C , 0.17 w/o uranium remained in the bed after 2.5 hr of fluorination.

Interpreting the results of these tests was complicated by the presence of the uranium fines in the packed-bed filter and by errors in sampling; nevertheless, on the basis of the rate of uranium removal, the results indicate that the reaction rate increases with the concentration of BrF_5 in the gas stream.

C. Fluorination Efficiencies for Runs BrR-1 to BrR-7

For Runs BrR-1 to BrR-7, fluorination efficiencies were calculated from the weight percent of uranium in the bed samples (see Table III). The initial uranium concentration in the bed was taken as 31.7 w/o (based on charged weight of alumina and UO_2). The efficiencies based on the reduction of BrF_5 to bromine and to BrF_3 were calculated.

TABLE III. Bed Concentrations and Fluorination Efficiencies

Run	Time, hr	Δt , hr	Concentration of U in Bed Sample, w/o	BrF_5 Feed During Δt , g	Fluorination Efficiency, % ^a	
					$\text{BrF}_5 \rightarrow \text{Br}_2$	$\text{BrF}_5 \rightarrow \text{BrF}_3$
BrR-1	2.17	2.17	0.0027	430	46.1	115.0
BrR-2	2.5	2.5	0.0047	610	32.5	81.2
BrR-3	0.5	0.5	0.83	290	70.7	176.8
	1.0	0.5	0.30	240	1.5	3.8
	1.5	0.5	0.18	160	0.5	1.3
	2.0	0.5	0.16	270	0.1	0.3
	2.5	0.5	0.17	175	0.0	0.0
BrR-4	1.0	1.0	6.40	385	43.8	109.5
	2.0	1.0	0.93	710	5.0	12.5
BrR-5	0.5	0.5	1.42	430	46.5	116.2
	0.83	0.33	1.54	420	0.0	0.0
BrR-6	0.58	0.58	0.29	700	29.7	74.3
BrR-7	0.5	0.5	4.62	960	18.7	46.8

^aFluorination efficiencies were calculated from the concentration of uranium in the fluid bed, assuming that the reduction in concentration is mainly due to chemical reaction. The effect of elutriation of uranium fines from the fluid bed on the uranium concentration was neglected.

For Run BrR-1 and during the initial portions of Runs BrR-3 to BrR-5, the fluorine efficiency based on the reduction of BrF_5 to BrF_3 exceeded 100%. We can therefore conclude that BrF_5 reduces to bromine in the fluorination of U_3O_8 .

D. Direct Fluorination of UO_2 Pellets

To determine the feasibility of direct fluorination of UO_2 pellets, three runs (BrR-10 to BrR-12) were made without the initial oxidation

step. The sintered, high-density UO_2 pellets were contacted with mixtures of BrF_5 and oxygen (see Table IV). Run BrR-10 was made at 300°C with 13.9 v/o BrF_5 in nitrogen (30 v/o oxygen); in Run BrR-11, the reaction temperature was increased to 410°C ; and in Run BrR-12, the BrF_5 concentration was increased to 18.6 v/o with temperature of 410°C .

TABLE IV. Processing Conditions for the Direct Fluorination of UO_2 Pellets with BrF_5

Column diameter: 1.5 in.
 Bed charge: 270 g of UO_2 pellets (0.5-in. diameter by 0.5 in. long)
 470 g of nominal 48 to 100 mesh alumina
 Pellet-bed depth: 2 in.
 Fluid-bed depth: 7 in. (static height)
 Diluent gas: Nitrogen

	BrR-10	BrR-11	BrR-12	BrR-14 ^a
Time, hr	2	2	2	2
Superficial gas velocity, ft/sec ^b	0.55	0.52	0.55	0.55
BrF_5 concentration, v/o	13.9	11.7	18.6	15.1
Oxygen concentration, v/o	30	30	27.2	31.2
Temperature, $^\circ\text{C}$	300	410	410	400
Total BrF_5 feed, g	810	600	1010	810
UO_2 reacted, g	5	49	46	227

^aBefore fluorination, the pellets were oxidized for 1 hr at 400°C with 30 v/o oxygen in nitrogen and a fluidizing-gas velocity at 0.5 ft/sec.

^bAt operating temperature and 1 atm pressure.

In BrR-10 (300°C), only 5 g of UO_2 reacted in 2 hr. Increasing the fluorination temperature to 410°C increased the quantity of UO_2 that reacted in 2 hr to 49 g (approximately 18% of the uranium charged). Further increasing the BrF_5 concentration to 18.6 v/o at 410°C did not increase reaction rate; only 46 g of UO_2 reacted. We expected the addition of oxygen to the BrF_5 gas stream to improve the fluorination rate by oxidizing the UO_2 to form U_3O_8 fines, which would then be more readily converted to UF_6 . However, the pellets remained intact and exhibited only a small weight loss. The surface of the pellets was scraped off to determine if a protective layer of fluoride formed which prevented oxidation of the pellets. An X-ray diffraction analysis of the scrapings indicated no uranium compound other than UO_2 . Apparently, BrF_5 in the oxygen inhibits oxidation of UO_2 .

In a fourth run (BrR-14), the processing sequence involved 1 hr of oxidation at 400°C with 30 v/o oxygen in nitrogen, followed by 2 hr of fluorination with a gas mixture consisting of 15.1 v/o BrF_5 and 31.2 v/o oxygen in nitrogen. During this run, 227 g of UO_2 pellets reacted. The

43 g of UO_2 pellet fragments recovered at the end of this run represented incomplete oxidation of the pellets to U_3O_8 . A comparison of Run BrR-14 with Run BrR-1 shows that the addition of oxygen to the BrF_5 does not markedly affect the rate of fluorination of U_3O_8 .

An additional run (BrR-15) was conducted in which oxidation and fluorination steps of various short time intervals were alternated (see Table V). The objectives of this test were:

1. To determine if UO_2 pellet oxidation would proceed after a fluorination period with BrF_5 . (The previous runs indicated that BrF_5 in oxygen inhibited oxidation.)
2. To improve fluidization by reducing the amount of U_3O_8 fines in the bed.
3. To investigate a method by which the overall oxidation and fluorination time might be reduced.

TABLE V. Operating Conditions for Test on Alternating Oxidation and Fluorination Periods (Run No. BrR-15)

Column diameter:	1.5 in.					
Bed charge:	274 g of UO ₂ pellets (0.43-in. diameter by 0.43 in. long) 470 g of nominal 48 to 100 mesh alumina					
Pellet-bed depth:	1 in.					
Fluid-bed depth:	7 in. (static height)					
Diluent gas:	Nitrogen					
Gas velocity:	0.45 to 0.50 ft/sec at 400°C and 1 atm					

	Run Time, hr					
	0 to 1.0	1.0 to 1.5	1.5 to 2.0	2.0 to 2.25	2.25 to 2.75	2.75 to 3.00
Oxygen concentration, v/o	34.0	-	34.2	-	32.6	-
Temperature, °C	415	-	400	-	400	-
<u>Fluorination</u>						
BrF ₅ concentration, v/o	-	14.6	-	7.9	-	13.7
Oxygen concentration, v/o	-	29.0	-	31.4	-	28.2
Temperature, °C	-	405	-	400	-	400
BrF ₅ feed, g	-	160	-	40	-	80

Both the oxidation and fluorination steps were conducted at 400°C. The concentration of oxygen in the feed gas was about 30 v/o during both steps. The BrF_5 concentration was 8 to 15 v/o during the fluorination.

There was no improvement in the amount of UO_2 reacted (215 g) by alternate oxidations and fluorinations, in comparison with Run BrR-14, in which 227 g of UO_2 were reacted after 1 hr of oxidation and 2 hr of fluorination. Thirty-two grams of UO_2 pellet fragments remained at the conclusion of Run BrR-15, indicating that the alternate oxidation-fluorination procedure resulted in a slight increase in oxidation of UO_2 to U_3O_8 fines.

We conclude that there would be no processing advantage by directly fluorinating UO_2 with BrF_5 . Fluorination rates are extremely low at temperatures less than 400°C .

E. Effect of Small Concentrations of BrF_5 in Elemental Fluorine

Holmes, Knudsen, and Vissers³ proposed that fluorination of U_3O_8 fines with elemental fluorine at low temperatures ($\sim 200^\circ\text{C}$) will proceed with the addition of small amounts of BrF_5 to the feed gas. Holmes *et al.* suggested the BrF_5 would react with U_3O_8 to form UF_6 with the reduction of the BrF_5 to Br_2 or BrF_3 ; the bromine compounds would then be refluorinated to BrF_5 , which would then continue the reaction to produce UF_6 .

Eight runs were made to demonstrate this effect. The runs were conducted in two steps: (1) oxidation of the UO_2 pellets to form U_3O_8 , and (2) fluorination to form UF_6 .

The first three runs (BrR-8, -9, and -13) were made with the off-gas filtered by the packed-bed filter. For the last five runs (BrR-17 to BrR-21), bayonet filters with blowback were installed in the disengaging section of the reactor. The bayonet filters prevented uranium fines from leaving the reactor; therefore, the fluorination was confined within the reactor. Previously, some fluorination of the elutriated fines continued in the packed-bed filter. The packed-bed filter was maintained at the same temperature as the fluid bed.

After the oxidation step for Run BrR-17, the bed was drained from the reactor to determine the extent of oxidation. The pellets were about 95% pulverized to U_3O_8 fines. X-ray diffraction of the remaining lumps (about 0.25 in. in diameter) showed them to be a mixture of U_3O_7 and U_3O_8 . The bed was then recharged to the reactor for fluorination. The oxidation temperature in subsequent runs was increased from approximately 400 to 450°C to promote a more complete pulverization of the pellets. (Run conditions are given in Table VI.)

TABLE VI. Operating Conditions for Study of Effect of Small Concentrations of BrF_5 in Fluorine

Column diameter: 1.5 in. Bed charge: 270 g of UO_2 pellets ^a 470 g of nominal 48 to 100 mesh alumina Pellet-bed depth: 1 in. Fluid-bed depth: 7 in. (static) Diluent gas: Nitrogen								
	BrR-8	BrR-9	BrR-13	BrR-17 ^a	BrR-18	BrR-19	BrR-20	BrR-21
Oxidation								
Time, hr	3	3	3	3	3	3	3	3
Superficial gas velocity, ft/sec ^b	0.5	0.5	0.5	0.5	0.54	0.54	0.54	0.54
Oxygen concentration, v/o	30	30	30	30	30	30	30	30
Temperature, $^\circ\text{C}$	400	400	410	410	460	460	460	450
Fluorination								
Time, hr	2	2	2	2	2	2	2	2
Superficial gas velocity, ft/sec ^b	0.56	0.55	0.5	0.5	0.56	0.55	0.55	0.49
BrF_5 concentration, v/o	1.3	-	2.0	2.1	2.2	-	-	2.6
Fluorine concentration, v/o	13.2	13.4	-	12.5	12.5	12.8	12.8	-
Temperature, $^\circ\text{C}$	200	195	200	200	200	200	200	200
Total BrF_5 feed, g	100	-	140	160	180	-	-	180

^a0.43-in.-diam by 0.43-in.-long UO_2 pellets for Run BrR-17; 0.5-in.-diam by 0.5-in.-long UO_2 pellets for all other runs.

^bAt operating temperature and 1 atm.

The fluorination steps of three runs (BrR-8, -17, and -18) were made with a mixture of BrF_5 (1.3 to 2.2 v/o) and fluorine (12.5 to 13.2 v/o), and the results were compared with the results from two runs (BrR-13 and -21), with BrF_5 (2.0 to 2.6 v/o) alone and three runs (BrR-9, -19, and -20) with fluorine (12.8 to 13.4 v/o) alone. The weight changes in the reactor are given in Table VII.

TABLE VII. Weight Changes in Reactor System in Studies on Effect of Small Concentrations of BrF_5 in Fluorine

	BrR-8	BrR-17	BrR-18	BrR-13	BrR-21	BrR-9	BrR-19	BrR-20
Fluorinating Agent	BrF_5 & F_2	BrF_5 & F_2	BrF_5 & F_2	BrF_5	BrF_5	F_2	F_2	F_2
Charge, g								
-14 +28 mesh alumina to reactor core	100	100	100	100	100	100	100	100
-48 +100 mesh alumina to reactor	470	470	470	470	470	470	470	470
-14 +28 mesh alumina to filter	100	-	-	100	-	100	-	-
Total Alumina	670	570	570	670	570	670	570	570
UO_2 pellets	268	272	270	264	269	268	270	270
(U_3O_8 equivalent)	(279)	(283)	(281)	(275)	(280)	(279)	(281)	(281)
Total Charge	938	842	840	934	839	938	840	840
Recovery at End of Run, g								
Final reactor bed	513	577	574	564	797	577	821	803
Total weight of samples	70	38	47	89	35	62	38	41
External filter chamber	128	-	-	239	-	235	-	-
Total	711	615	621	892	832	874	859	850
Net uranium compounds volatilized, assuming compounds were U_3O_8	238	238	230	53	18	75	0	1

The net uranium volatilized for Runs BrR-8, -17, and -18, where the reagent gas consisted of both fluorine and a low concentration of BrF_5 , are in close agreement, even though Run BrR-8 was made with the separate filter chamber in the off-gas line from the reactor.

For Runs BrR-19 and -20, in which only fluorine was used, the final bed weight indicated a negligible UF_6 production. In Run BrR-9 (with the filter external to the reactor), 75 g of U_3O_8 was volatilized as UF_6 . The conditions for Runs BrR-9, -19, and -20 were essentially identical. There is no reasonable explanation for the difference in UF_6 formation for these runs, in terms of either temperature effects or fluidization quality. In any case, the basic conclusion is not affected.

In Run BrR-13, the fluorination was conducted with 2.0 v/o BrF_5 and no fluorine, and 53 g of U_3O_8 reacted to form UF_6 . In Run BrR-21, for similar run conditions, 18 g of U_3O_8 had volatilized.

The amount of U_3O_8 fluorinated to UF_6 with fluorine and with BrF_5 individually was not equivalent to the amount of fluorination by the mixture of BrF_5 and fluorine. We therefore conclude from these eight tests that a small amount of BrF_5 has a promotional effect on low-temperature fluorination with elemental fluorine.

F. Effect of a Small Concentration of Fluorine in BrF₅

One run was made (BrR-16) to determine if a small amount of fluorine in BrF₅ would increase the fluorination rate of U₃O₈. After the oxidation step, the bed was fluorinated with 49.2 v/o BrF₅ and 5.7 v/o fluorine in nitrogen (see Table VIII for run conditions). We intended to carry out the fluorination at 200°C. However, upon introduction of the BrF₅ and fluorine, the reactor temperature began to rise. The column heaters were shut off, and cooling air was introduced on the reactor surface. After 15 min. of operation, the column temperature attained a maximum of 290°C. Within 20 min, the temperature returned to 210°C. The fluorination was completed within 35 min.

TABLE VIII. Run Conditions for Fluorination of U₃O₈ with a Low Concentration of Fluorine in BrF₅ (Run BrR-16)

Column diameter:	1.5 in.
Bed charge:	280 g UO ₂ pellets (0.43-in. diameter by 0.43-in. long) 470 g of nominal 48 to 100 mesh alumina
Pellet-bed depth:	1 in.
Fluid-bed depth:	7 in. (static height)
Diluent gas:	Nitrogen
<hr/> <u>Oxidation</u>	
Time, hr	3
Superficial gas velocity, ft/sec ^a	0.5
Oxygen concentration, v/o	30
Temperature, °C	410
<hr/> <u>Fluorination</u>	
Time, min	35
Superficial gas velocity, ft/sec ^a	0.43
BrF ₅ concentration, v/o	49.2
Fluorine concentration, v/o	5.7
Temperature, °C	210 to 290
Total BrF ₅ feed, g	880

^aAt operating temperature and 1 atm pressure.

No bed caking occurred, and the alumina bed was easily drained from the reactor at the end of the run. The final bed contained 6.8×10^{-2} w/o uranium and an additional 2 g of unreacted pellets. In comparison, the uranium concentration in the final bed was 0.29 w/o for Run BrR-6 (40.5 v/o BrF₅). However, because of the initial temperature rise in the run (BrR-16) and the higher BrF₅ concentration (49.2 v/o), the effect of the

addition of a small concentration of fluorine is not certain. Additional experimentation would be necessary to verify any improvement in the fluorination rate.

IV. CONCLUSIONS

1. The lowest fluorination temperature with BrF_5 for practical operation is 200°C .
2. The rate of fluorination increases with the concentration of BrF_5 in the range of 10 to 50 v/o BrF_5 in nitrogen.
3. Direct fluorination of UO_2 pellets with a mixture of 10 to 20 v/o BrF_5 and 30 v/o oxygen in nitrogen at 300 to 400°C essentially does not proceed.
4. A small concentration of BrF_5 (1 to 2 v/o) acts as a promoter for fluorination of U_3O_8 with elemental fluorine at low temperatures ($\sim 200^\circ\text{C}$).
5. A 3-hr run, consisting of alternate oxidations and fluorinations, results in a slight increase in oxidation of UO_2 to U_3O_8 fines and a slight decrease in the fluorination of the U_3O_8 to UF_6 , in comparison to another 3-hr run consisting of 1 hr of oxidation followed by 2 hr of fluorination.
6. The fluorination with BrF_5 proceeds smoothly in a fluid-bed reactor. No bed caking was observed in any of the runs.

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