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FLUID-BED CONVERSION OF URANIUM TETRAFLUORIDE  
TO URANIUM HEXAFLUORIDE

by

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## TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	3
I. SUMMARY . . . . .	3
II. INTRODUCTION . . . . .	4
III. EXPERIMENTAL . . . . .	5
Materials . . . . .	5
Equipment. . . . .	7
Operating Procedure. . . . .	9
IV. RESULTS AND DISCUSSION . . . . .	10
Refined Uranium Tetrafluoride . . . . .	10
Rand Acid-leached Uranium Tetrafluoride . . . . .	12
Anaconda Acid-leached Uranium Tetrafluoride . . . . .	15
Anaconda Carbonate-leached Uranium Tetrafluoride. . . . .	16
Recovery and Product Purity . . . . .	17
Operability and Process Improvements . . . . .	19
V. ACKNOWLEDGMENTS . . . . .	20
VI. APPENDICES . . . . .	21
A. Melting and Boiling Points of Some Fluorides Anticipated in the Fluorination of Crude Uranium Tetrafluoride. . . . .	21
B. Fluorine Efficiency. . . . .	22
Method of Calculation . . . . .	22
Gas Analysis Check on the Calculation. . . . .	23
VII. BIBLIOGRAPHY . . . . .	25

# THE FLUID-BED CONVERSION OF URANIUM TETRAFLUORIDE TO URANIUM HEXAFLUORIDE

by

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## ABSTRACT

Experiments conducted in a  $2\frac{1}{2}$ -inch diameter reactor have demonstrated that the continuous fluorination of uranium tetrafluoride to hexafluoride with elemental fluorine in a fluidized bed is possible. Practicable fluorine efficiencies and conversion rates were attained with good temperature control in experiments with refined uranium tetrafluoride. Runs made with crude uranium tetrafluoride, derived from the reduction and hydrofluorination of ore concentrates produced by the acid-leach process, indicated that these also can be processed at satisfactory rates and efficiencies. Uranium tetrafluoride derived from carbonate-leached ore concentrate gave a lower production rate and was more difficult to process because of sintering tendencies.

## I. SUMMARY

In this report are discussed the experimental results obtained in the fluorination of uranium tetrafluoride to the hexafluoride with elemental fluorine in a 2.5-inch diameter, continuously fed fluidized-bed reactor. Four types of uranium tetrafluoride were fluorinated: refined green salt, and crude uranium tetrafluorides derived from the reduction and hydrofluorination of South African (Rand) acid-leached, Anaconda acid-leached, and Anaconda carbonate-leached ore concentrates. Refined uranium tetrafluoride was used for the shake-down tests on the reactor and to obtain data on the effects of temperature, bed height, fluidizing gas velocity, fluorine concentration, and inert solid diluent. For uranium tetrafluoride derived from Rand ore, data were obtained on fluorine utilization, production rates, and buildup of impurities in the bed. Exploratory fluorination rate runs were made on the tetrafluorides derived from the two types of Anaconda ore concentrates. Some data were obtained on the exhaustive fluorination of the ash to reduce the uranium to levels of less than one per cent.

Fluorination experiments with refined uranium tetrafluoride showed that the efficiency of utilization of the fluorine increased with temperature over the range studied, 300 to 450 C. Efficiencies over 85 per cent (15 per cent of fluorine unreacted) were obtained at 400 C. Dilution of the bed with solids inert to fluorine reduced the fluorine efficiency markedly. Dilution of the fluorine with nitrogen below the 25 volume per cent used in most of the runs decreased the fluorine efficiency slightly, but the velocity of the gas had no effect at 400 C. Bed height did not affect the efficiency at 400 C, but at 350 C increased efficiency was obtained with increasing bed height. Production rates above 100 pounds uranium hexafluoride per (hour) (cubic foot of bed) were attained easily with 25 per cent fluorine in the inlet gas.

Exploratory experiments with crude uranium tetrafluoride made from South African (Rand) ore concentrate showed that reasonable fluorine efficiencies and production rates could be achieved at 400 and 450 C. One run with Anaconda acid-leached uranium tetrafluoride indicated that production rates were comparable to those of the Rand acid-leached uranium tetrafluoride. Anaconda carbonate-leached uranium tetrafluoride in one run showed a substantially poorer production rate.

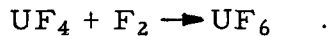
## II. INTRODUCTION

Ore concentrate, produced in the mining and milling of uranium ore, represents a material containing 50 per cent or more uranium and a considerable amount (1 to 10 per cent) of metallic impurities. Currently much of this uranium is converted to uranium hexafluoride which is the feed for the  $U^{235}$ - $U^{238}$  diffusion separation plant. In the processing to uranium hexafluoride essentially all of the metallic impurities must be removed prior to isotopic enrichment by gaseous diffusion.

The conventional route for producing pure uranium hexafluoride from ore concentrate has been to dissolve the concentrate in nitric acid, free the uranium from the metallic impurities by solvent extraction, concentrate the pure uranyl nitrate, denitrate to form the trioxide, then reduce, hydrofluorinate and fluorinate the uranium to uranium hexafluoride. In the new process developed by Argonne National Laboratory, the ore concentrate is reduced without prior treatment except physical sizing. The resulting uranium dioxide is hydrofluorinated and then fluorinated. Most metallic impurities are removed as an ash from the fluorination reactor. However, some volatile fluorides are formed, primarily those of molybdenum and vanadium, and these must be removed by distillation to obtain a pure uranium hexafluoride for the gaseous diffusion process. A summary of fluorides that can be present and their boiling and melting points are given in Appendix A.<sup>(7)</sup>

Studies on the pilot plant reduction and hydrofluorination reactions have been completed and are reported elsewhere.<sup>(2,4)</sup> Some data have also been reported on the distillative separation of molybdenum and vanadium hexafluorides from uranium hexafluoride.<sup>(5)</sup> The fluorination study is reported here.

The over-all fluorination reaction is as follows:



Rate data on this reaction,<sup>(3)</sup> obtained with a thermobalance, indicate that it does not proceed at an appreciable rate below 200 C. At higher temperatures, however, the rate is rapid and temperature-dependent. The temperature dependence obeys the Arrhenius relationship, yielding an activation energy of 19 to 20 kcal per mole. The rate is not affected by gas velocity, but is proportional to the fluorine concentration.

Fluorination of pure uranium hexafluoride on a production scale is currently carried out in vertical tower, flame reactors. Attempts to operate such reactors with impure uranium tetrafluorides have not been successful because of impurity scaling on the wall. The present study is concerned with the demonstration of the use of a fluidized bed for fluorination of these crude tetrafluorides. The use of the fluidized-bed principle for this gas-solid reaction offers good temperature control with good heat transfer rates, and avoids the high temperatures which cause impurity fusion.

### III. EXPERIMENTAL

#### Materials

The materials used in these tests were fluorine, nitrogen, and uranium tetrafluorides, including those obtained from Anaconda acid-leached ore, Anaconda carbonate-leached ore and Rand acid-leached ore, as well as the refined tetrafluoride.

The chemical compositions and the physical properties of the various tetrafluorides that were fluorinated are given in Tables 1 and 2, respectively. Processing history of the tetrafluorides varied.

The acid-leached uranium tetrafluorides were obtained by an acid leach of the ore, precipitation of uranium as ammonium diuranate and calcination of uranium trioxide. The carbonate-leached uranium tetrafluoride was obtained by solubilizing the uranium in the ore with sodium carbonate and precipitating it as sodium diuranate with sodium hydroxide.

Table 1

CHEMICAL COMPOSITION OF GREEN SALT FROM  
VARIOUS SOURCES

Green Salt Source	UF <sub>4</sub> (%)	UO <sub>2</sub> (%)	UO <sub>2</sub> F <sub>2</sub> (%)	Total Uranium (% by weight)	Metallic Impurities, Weight Per Cent <sup>a</sup>				
					Above 1%	1 0 to 0 1%	0 1 to 0 01%	0 01 to 0 001%	Below 0 001%
Rand Acid-leach Ore	80 4	3 3	6 2	68	Ca(1 5), Na(1 6)	Fe(0 4), V(0 15)*, Cu(0 5)	Al, K, Mg, Mn, Pb, P, Ni	Li, Sr, Cr, Zr, Zn, Mo(0 0005)*	
Anaconda Acid-leach Ore	93 1	0 6	1 3	72	None	Na(0 2),* Ca(0 1), Fe(0 6), Mg(0 1)	Al	Cu, K, Mn, Ni, P, Pb, Ti, Zn, Si, Mo(0 002)*	
Anaconda Carbonate-leach Ore	74 0	3 0	3 9	65 8	Na(7)*	K(0 5), Pb(0 1), Al(0 15), Fe(~0 2), Ca(0 4), Mg(~0 01)	Sr(0 015), Mn(0 01), V(0 058), S(0 02), Ni(~0 05), Si(0 02), Ba(0 06), Cr(0 015)		Mo(0 00007)*
"Refined" Green Salt	94 6	3 9	1 5	76 9	None	None	None	None	

<sup>a</sup> Impurity amounts were obtained by spectrographic analysis (factor of 2 accuracy) except for those marked with an asterisk, which were obtained by wet analysis. A number in parentheses is the result of analysis.



Table 2  
PHYSICAL PROPERTIES OF GREEN SALT

Green Salt	Bulk Density <sup>a</sup> (g/cc)	Pack Density (g/cc)	Particle Size Distribution: % in Indicated Size Range						
			+20 <sup>b</sup>	-20 to +40	-40 to +60	-60 to +100	-100 +200	-200 +325	-325
Rand Ore	1.82	2.07	0.1	8.0	32.4	30.5	18.3	9.0	1.7
Anaconda Acid Leach	2.50	2.90	0.10	0.2	6.9	31.0	34.6	19.7	6.9
Anaconda Carbonate Leach	2.50	2.75	0.10	2.2	17.6	37.2	24.9	11.1	1.9
"Refined" Green Salt	3.17	3.46	0.02	6.9	35.5	33.6	19.8	3.2	1.0

<sup>a</sup>Based on 100 ml volume of solids

<sup>b</sup>Mesh, U. S. Sieve Series

The oxide from the acid-leach process and the sodium diuranate from the carbonate-leach process were reduced and hydrofluorinated in pilot plant fluidized-bed reactors to produce the uranium tetrafluorides for the study. The reduction was done at a maximum temperature of 1100 F, the hydrofluorination at 850 F. The hydrofluorinated product from the sodium diuranate is actually a sodium uranium fluoride compound, but, for convenience, this and the other hydrofluorination products are referred to as uranium tetrafluorides. The uranium tetrafluoride products derived from ore concentrates will be designated by the name of the mill and the type of concentration process used. The "refined" uranium tetrafluoride was obtained by solvent extraction of a nitric acid solution of the ore concentrate and calcination of the nitrate product to uranium trioxide. This oxide also was reduced and hydrofluorinated in the pilot plant fluidized-bed reactors.

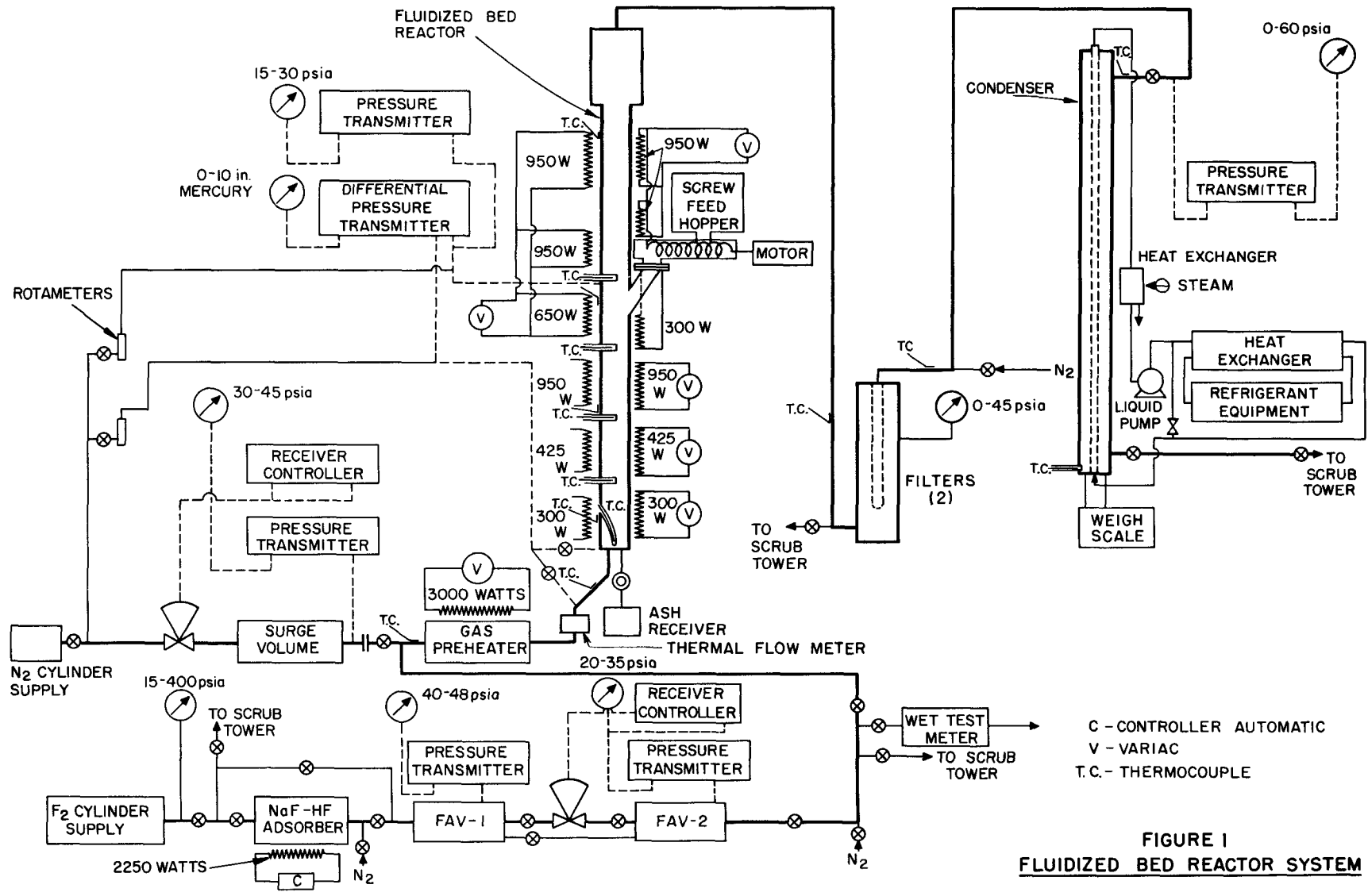
The fluorine was obtained from General Chemical Company in six-pound cylinders and was guaranteed to contain a minimum of 98.5 per cent fluorine. Impurities were mostly nitrogen with minor amounts of oxygen, carbon tetrafluoride, carbon dioxide and hydrogen fluoride.

Nitrogen was obtained from Liquid Carbonic and was guaranteed to contain greater than 99.6 per cent nitrogen.

The calcium fluoride used as a bed diluent in some tests was a commercial grade, crystalline material which was crushed and screened to obtain a 30 to 100 mesh fraction. This had a bulk density of 1.7 g/ml.

### Equipment

The equipment for the pilot plant can be classified into the gas-metering system, the reactor system, and the condensing system. A simplified flow diagram is shown in Figure 1.



**FIGURE 1**  
**FLUIDIZED BED REACTOR SYSTEM**

Fluorine and nitrogen flows to the reactor were measured by orifices, the pressure being transmitted by Taylor pneumatic instruments. The fluorine flow rate could also be determined by noting pressure drop in a 17.6-cu ft hold tank. Both flows were regulated automatically.

The reactor system consisted of the gas preheater, reactor, and filters. The reactor was  $2\frac{1}{2}$  inches in diameter, 4 feet long, topped by a six-inch diameter disengaging section, 12 inches long. The inlet gas distributor contained inverted cone holes with  $\frac{1}{16}$ -inch openings at the tip of the 45-degree cone. Pressure in the reactor and pressure drop across the bed were indicated by gages connected to pressure taps. Three inside and five skin thermocouples were provided. Heat was supplied by clam-shell Nichrome wire heaters, the bottom one controlled automatically, the others by variable voltage transformers. No method for cooling the reactor was provided except for removal of insulation. Uranium tetrafluoride was fed into the reactor by a one-inch screw driven by a direct-current motor. Screw revolutions were automatically counted. The rate of powder fed could be determined by watching the change in level of powder in a one-inch diameter Fluorothene sight glass. Bed height could be determined by three movable thermocouples in the central thermowell. The two filter units, separate from the reactor and equipped for blowback, contained sintered Monel elements of 10-micron pore size.

The condenser system included a 10-foot long, three-inch diameter condenser fitted with a fin-type cooling unit consisting of 12 fins mounted on  $\frac{3}{4}$ -inch tubing parallel to the tube axis. Inside this tubing circulated trichloroethylene which was cooled by a Freon-12, three-horsepower refrigeration system. The trichloroethylene could be heated to 90 C by a steam heat exchanger when it became necessary to vaporize the uranium hexafluoride from the condenser. The condenser was placed on a tared 50-pound scale.

### Operating Procedure

The general procedure for making a run is discussed below. Departures from this procedure are mentioned in the discussion of results when the change of procedure affected the outcome of a run.

Preliminary data on the pressure drop and fluidization characteristics of the various green salts with or without calcium fluoride were first obtained in a glass column using air as the fluidizing medium.

To start a fluorination run in the metal reactor, nitrogen sufficient to fluidize the uranium tetrafluoride was passed through the reactor. If enough uranium tetrafluoride had not been added already, it was screw-fed into the reactor to the desired bed height. After the bed had been heated to temperature, the fluorine was introduced and the uranium tetrafluoride

screw feeder was started. Rate of uranium hexafluoride production was determined by moving the three thermocouples in the bed to determine the bed interface. Duration of runs varied but generally consisted of operating for two hours at some equilibrium condition.

Samples of the feed material were examined chemically and physically. The residue at the end of a run was often analyzed. Hydrolyzed samples of the gas passing into the condenser were examined spectrographically to determine the amount of impurities in the uranium hexafluoride (for ore concentrate uranium tetrafluoride runs only). Off-gas from the condenser was sampled by drawing the gas into an evacuated bulb and analyzing for fluorine and/or uranium. The fluorine concentration was determined to ensure that no gross error had been made in measuring the fluorine efficiency and the uranium content was measured to determine the effectiveness of the condenser.

With refined uranium tetrafluoride the effect on fluorine utilization efficiency of changes in bed height, fluorine concentration, fluidization gas velocity temperature and bed diluent were determined. With uranium tetrafluoride from ore concentrates the fluorine efficiency and production rate at different temperatures were determined, using calcium fluoride diluent in some cases. In addition, the extent of impurity buildup in the bed was determined for uranium tetrafluoride derived from some of the ore concentrates. Data were also obtained on the completeness of removal of uranium from the ash.

#### IV. RESULTS AND DISCUSSION

##### Refined Uranium Tetrafluoride

With refined uranium tetrafluoride the fluorine efficiency\* increased markedly with increasing temperature, decreased with solid diluent in the bed and changed little with the fluorine concentration over the range studied. High fluorine efficiencies, above 90 per cent, were attained at 400 C with 25 per cent fluorine in the inlet fluidizing gas (Figure 2). Fluorine efficiencies of 100 per cent are not required in this process as, after the uranium hexafluoride has been removed, the waste gas containing the unreacted fluorine can be reacted with uranium tetrafluoride to form an intermediate uranium fluoride, which can be fed into the reactor. Thus, no fluorine is lost in the over-all process. When calcium fluoride diluent is present in

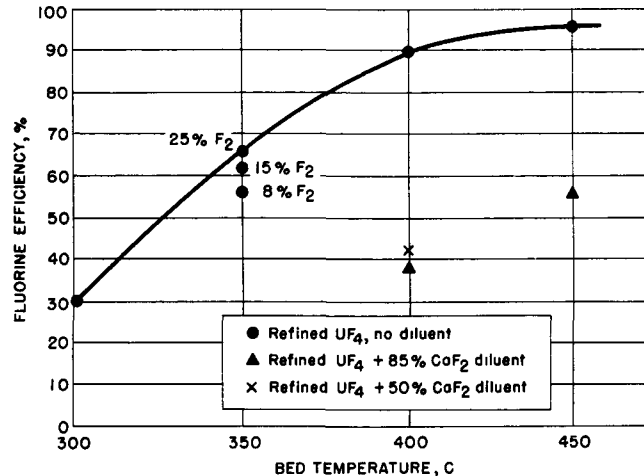
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\*Fluorine efficiency (F. E.) is defined as the ratio of the amount of fluorine required to produce the uranium hexafluoride collected in the condenser to the amount of fluorine entering the reactor. A sample calculation for fluorine efficiency is shown in Appendix B.

Figure 2

EFFECT OF TEMPERATURE, FLUORINE CONCENTRATION,  
AND BED DILUTION ON FLUORINE EFFICIENCY

Conditions: Inlet gas, 25% fluorine (or as indicated)  
Gas velocity, 0.5 ft/sec.  
Bed height - dumped - diluent runs, 8.5 inches;  
                  other, 11 inches



concentrations of from 50 to 85 per cent, the fluorine efficiency was approximately halved (Figure 2). The use of lower fluorine concentration in the inlet fluidizing gas decreased the fluorine efficiency only slightly in tests made at 350 C with inlet fluorine concentrations of 8, 15 and 25 per cent.

An increase in the amount of uranium in the fluidized bed (i.e., greater bed height) increased the fluorine efficiency at 350 C but at 400 C, where high efficiency is already attained, little effect was noted (Table 3). The lower efficiency with the smallest bed heights was partly due to the low (25 C) temperature of the gas entering the reactor. Temperatures below the reaction temperature were measured in the bottom inch of bed. The gas velocity in the reactor in the range from 0.32 to 0.52 feet/sec did not affect the fluorine efficiency at 400 C (Table 3).

Reaction rates in excess of 150 pounds of uranium hexafluoride per (cubic foot of dumped bed)(hour) were achieved without difficulty. In any scale up of the process the rate of heat removal may limit the reaction rate per unit volume of bed.

Table 3

EFFECT OF BED HEIGHT AND FLUIDIZATION VELOCITY ON  
FLUORINE EFFICIENCY PRODUCTION RATES FOR  
REFINED URANIUM TETRAFLUORIDE UNDER  
DIFFERENT CONDITIONS

Run No.	Temp (C)	Weight of Dumped Bed (lb) <sup>a</sup>	Bed Height to Diameter Ratio	Fluorine Efficiency (%)	Gas Velocity (ft/sec) <sup>b</sup>	Inlet Gas Fluorine Conc (%)	Production Rate lb UF <sub>6</sub> (hr)(cu ft of dumped bed)
1	350	1.76	2.3	15	0.52	25.8	71
2	350	2.82	3.5	38	0.50	26.6	114
3	350	4.36	4.5	65	0.47	25.0	147
4	350	5.19 <sup>c</sup>	6.5	82	0.47	25.8	127
5	400	4.95	6.6	91	0.53	24.8	134
6	400	2.57 <sup>c</sup>	4.6	90	0.51	24.7	204
7	400	2.57 <sup>c</sup>	4.6	90	0.32	31.1	151
8	400	4.64	6.6	86	0.42	25.9	106
9	400	4.96	7.0	91	0.53	24.9	128

<sup>a</sup> Bed density varied but was approximately 119 lb/cu ft at 350 C and 106 lb/cu ft at 400 C

<sup>b</sup> At reactor conditions

<sup>c</sup> Estimated from differential pressure drop across the bed

### Rand Acid-leached Uranium Tetrafluoride

Initial exploratory experiments on processing Rand acid-leached uranium tetrafluoride consisted of fluorination runs with small amounts of uranium in a bed of inert solids to simulate conditions when large amounts of inorganic ash are in the bed. Later, runs were made with undiluted Rand material at a constant bed height and no solids take off.

Reasonable fluorine efficiencies and uranium hexafluoride production rates were obtained with large quantities of inorganic fluorides present in the fluidized bed (Table 4). Data were obtained with inert calcium fluoride diluent in the bed to simulate conditions existing in the bed when the inorganic fluorides present in the Rand feed build up in the bed. The starting bed for each run was 100 per cent calcium fluoride to which uranium tetrafluoride was fed at a rate such that there was no buildup of uranium tetrafluoride in the bed, i.e., the feed rate equaled the conversion rate. Efficiency increased from 38 per cent at 450 C to 68 per cent at 550 C. Production rates of 134 pounds of uranium hexafluoride per (cubic foot)(hour) were obtained at 550 C. The operating limits of the present reactor were exceeded in a 600 C run because sufficient cooling was not available to control the reaction temperature.

Table 4

EFFECT OF TEMPERATURE ON FLUORINE EFFICIENCY AND  
ON URANIUM HEXAFLUORIDE PRODUCTION FOR  
LOW-URANIUM CONCENTRATION BEDS

Conditions: Inlet F<sub>2</sub> concentration, 30%  
Superficial gas velocity, 0.47 ft/sec  
Bed height, 9 in.  
Starting bed, 100% CaF<sub>2</sub>  
Feed material, Rand acid-leached UF<sub>4</sub>

Run No.	Temp (C)	Maximum UF <sub>6</sub> Product Rate [lb/(cu ft)(hr)]	Fluorine Efficiency at this Rate (%)	Uranium in Bed at End of Run (%)
F-21	450	75	38	Not Determined
F-22	500	96	49	2.35
F-23	550	134	68	Not Determined
F-24	600	Ignition	Ignition	3.9

Other runs were made with no calcium fluoride diluent in the bed (i.e., the initial bed was 100 per cent Rand uranium tetrafluoride to which additional material of the same composition was fed to maintain a constant bed height with no ash take off). The bed of 100 per cent Rand uranium tetrafluoride was first fluorinated at 350C for two hours, since experience had shown that initial control of the temperature was difficult because of lack of cooling facilities. After this two-hour period the bed temperature was increased to the desired value. Fluorination was continued until a relatively low uranium hexafluoride production was attained. Data from these runs showed:

1. The bulk density of the bed decreases due to the buildup of the inorganic ash. Data from a 400 C run (Figure 3) show the decrease in bed density as indicated by the decrease in pressure drop through the constant height bed. Particle size distribution, bulk, and pack density are given in Table 5.
2. The uranium hexafluoride production decreases as the amount of uranium in the bed decreases, due to the accumulation of inorganic fluoride ash (Figure 3 and Table 5).
3. Relatively high sodium contents in the bed, at least 22 per cent, can be tolerated without caking. This is important since sodium combines with uranium tetrafluoride to form relatively low melting compounds, e.g., 3NaF · UF<sub>4</sub>, mp 629 C.<sup>(1)</sup> Sodium composition of the beds at 400 and 450 C are given in Table 6, along with the composition of other elements.

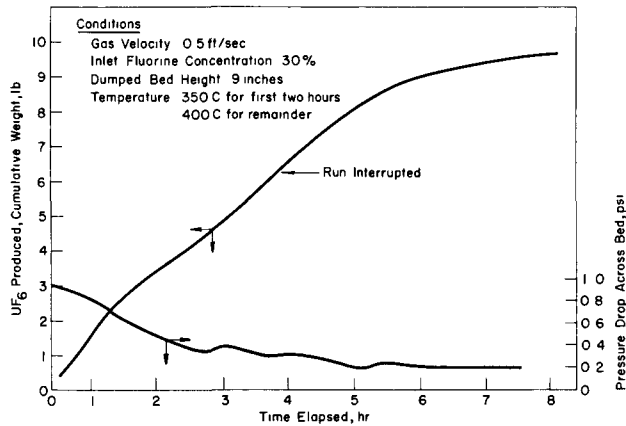


Figure 3

Fluid-bed Fluorination of Uranium Tetrafluoride: Effect of Run Time on Production of Uranium Hexafluoride and on Bed Density

Table 5

CHANGE IN PARTICLE SIZE AND DENSITY OF FLUIDIZED BED DURING FLUORINATION

Conditions: Temp: 400 C  
Velocity: 0.5 ft/sec  
Inlet F<sub>2</sub> Conc: 15%  
Feed: Rand Acid-leached

Particle Size Distribution  
(% in Indicated Size Range)

U.S. Standard Mesh	Initial	After 4 hr <sup>a</sup>	After 9 hr <sup>a</sup>
+20	0.05	0.1	1.8
-20 +40	8.0	13.1	11.9
-40 +60	32.4	37.3	32.2
-60+100	30.5	31.8	27.3
-100+200	18.3	10.3	11.8
-200+325	9.0	5.5	14.1
-325	1.7	2.0	0.9

Density

Bulk, g/cc	1.82	1.07	0.66
Pack, g/cc	2.08	1.50	1.08
Bed Weight, g	1350	715	407
Dumped Height, <sup>b</sup> inches	9.4	8.5	7.8

<sup>a</sup> Includes 2 hr at 350 C

<sup>b</sup> Height =  $\frac{\text{Weight of Bed}}{\text{Bulk Density} \times \text{Cross-sectional Area of Reactor}}$



Table 6

COMPOSITION OF FLUIDIZED BED DURING  
FLUORINATION RUNS<sup>b</sup>

Conditions: 15 per cent fluorine in inlet gas  
Bed height, approximately 9 inches  
Gas velocity at operating conditions, 0.5 ft/sec

Weight per cent of component<sup>b</sup>

Component	Composition of Rand Acid-leach Feed	400 C Run		450 C Run	
		After 4 hr <sup>a</sup>	After 10 hr <sup>a</sup>	After 4 hr <sup>a</sup>	After 7 hr <sup>a</sup>
U	68	48.8	26.0	31.3	18.5
H <sub>2</sub> O Solubles	6.5	16.8	8.8	9.1	8.1
Na	1.6	10.5	20.0	18	22
Mo	0.0005	0.02	0.02	0.0004	0.0004
V	0.15	0.2	0.5	0.26	0.36
Ca	1.5	2	5	5	5
Cu	0.5	1	2	2	2
Fe	0.4	1.5	2	2.5	2.5
K	0.1	1	2	2	2
Mg	0.04	0.2	1	0.5	0.5
Ni	0.01	0.05	0.1	0.1	0.05
Ti	0.0005	0.04	0.05	0.05	0.05

<sup>a</sup> Includes 2 hr at 350 C.

<sup>b</sup> Impurity analyses were by spectrographic methods (factor of 2 accuracy) except for sodium and some molybdenum and vanadium analyses, which were analyzed by wet methods.

Anaconda Acid-leached Uranium Tetrafluoride

Anaconda acid-leached uranium tetrafluoride appears to be as reactive as the Rand uranium tetrafluoride (see Table 7). The comparison runs were at different gas velocity, fluorine concentrations and starting temperatures; based on the pounds of uranium hexafluoride produced per cubic foot of fluorine passing through the bed, however, the uranium tetrafluorides show similar reactivities. At lower temperatures, 300 to 350 C, severe caking was encountered with the Anaconda acid-leached uranium tetrafluoride, but this might be avoided by slightly higher gas velocity.

Table 7

COMPARISON OF URANIUM HEXAFLUORIDE PRODUCTION FOR  
RAND ACID-LEACHED AND ANACONDA ACID-LEACHED  
URANIUM TETRAFLUORIDE

Conditions	Rand		Anaconda	
	3 hr at 350 remainder 400		400	
Temp, C	3 hr at 350 remainder 400		400	
Fluorine in Nitrogen, %	15		36	
Gas velocity, ft/sec	0 50		0 36	
Dumped bed height, in	10		10	
	Rand Acid-leached UF <sub>4</sub>		Anaconda Acid-leached UF <sub>4</sub>	
	Cumulative weight UF <sub>6</sub> Produced		Cumulative weight UF <sub>6</sub> Produced	
At End of	(lb)	(lb UF <sub>6</sub> /cu ft F <sub>2</sub> )	(lb)	(lb UF <sub>6</sub> /cu ft F <sub>2</sub> )
2 hr	3 38	0 386	6 53	0 459
4 hr	6 57	0 392	10 28	0 361
6 hr	8 88	0 355	-	-
8 hr	9 86	0 296	-	-

Anaconda Carbonate-leached Uranium Tetrafluoride

Data from one run on Anaconda uranium tetrafluoride show that the rate of uranium hexafluoride production is much lower than with the Rand uranium tetrafluoride. Results are shown in Table 8

Table 8

COMPARISON OF URANIUM HEXAFLUORIDE PRODUCTION FOR  
RAND ACID-LEACH AND ANACONDA CARBONATE-LEACH  
URANIUM TETRAFLUORIDE

Conditions	Temp 2 hr at 350 C followed by 6 hr at 400 C			
F <sub>2</sub> in inlet gas	30% for Anaconda carbonate-leach 15% for Rand acid-leach			
Fluidizing gas velocity	0 5 ft/sec			
Bed height	10 inches			
	Anaconda Carbonate-leach UF <sub>4</sub>		Rand Acid-leach UF <sub>4</sub>	
	Cumulative weight UF <sub>6</sub> Produced		Cumulative weight UF <sub>6</sub> Produced	
At End of	(lb)	(lb UF <sub>6</sub> /F <sub>2</sub> )	(lb)	(lb UF <sub>6</sub> /F <sub>2</sub> )
2 hr	1 44	0 088	3 38	0 386
4 hr	4 65	0 149	6 57	0 392
6 hr	5 72	0 123	8 88	0 355
8 hr	6 54	0 116	9 68	0 296

Samples of the bed showed that sodium content increased to approximately 50 per cent, based on spectrographic analysis (Table 9). At this sodium level some sintering occurred at the distributor.

Table 9

BED ANALYSIS FOR ANACONDA CARBONATE-LEACH RUN

Component	Analysis, wt %		
	Feed	After 4 hr <sup>a</sup>	After 8 hr <sup>a,b</sup>
U	65.8	22.2	15.6
H <sub>2</sub> O Solubles	-	11.4	-
Na	10	Very Strong	50
Al	0.15	0.15	0.6
Mo	0.00007 <sup>c</sup>	0.0009 <sup>c</sup>	Not Analyzed
V	0.058 <sup>c</sup>	0.14 <sup>c</sup>	0.6
Ba	0.06	0.15	0.2
Ca	0.4	1	2
Cu	-	0.5	1
Cr	0.015	0.015	0.02
Fe	0.2	0.4	0.6
K	0.5	2	5
Mn	-	-	0.1
Mg	0.1	0.4	6
Ni	0.05	0.05	0.04
Pb	0.1	0.1	0.15
Sr	0.015	0.015	0.04
Bulk Density of Bed, gm/cc	2.50	0.725	0.85

<sup>a</sup> Includes 2 hr at 350 C.

<sup>b</sup> Ten per cent sintered.

<sup>c</sup> Wet analyses. All others by spectrographic analysis, factor of 2 accuracy.

Recovery and Product Purity

As was expected, the fluorides of molybdenum and vanadium were found in the product fractions (Table 10). These were the only impurities found whose volatilities require the use of fractional distillation for separation from uranium hexafluoride.

Table 10

MOLYBDENUM AND VANADIUM FOUND IN  
PRODUCT URANIUM HEXAFLUORIDE<sup>a</sup>

UF <sub>4</sub> Processed	Analysis of Gas Sample Taken During Run (ppm) <sup>b</sup>		Liquid Sample of Product (ppm) <sup>b</sup>	
	Mo	V	Mo	V
Rand Acid-leached	17	1470	17	677
Anaconda Carbonate-leached	Gas Not Sampled		~0.8	1130

<sup>a</sup> Feed Analysis (parts per million parts uranium): Rand - Mo 7, V 2200; Anaconda - Mo ~1, V 882.

<sup>b</sup> Based on uranium.

Since the non-volatile ash must be purged from the reactor to keep the sodium which promotes sintering at a low level, it was of interest to determine whether the uranium in the ash could be removed by fluorination to levels of less than one per cent uranium. Data on removal of uranium from ash of both Rand and Anaconda uranium tetrafluoride runs are given in Table 11. The uranium content of the ash was reduced to less than one per cent in 5 to 6 hours of fluorination at temperatures between 400 and 600 C with 30 per cent fluorine in nitrogen.

Table 11

REMOVAL OF URANIUM BY FLUORINATION OF  
REACTOR ASH

Conditions: Fluorine Concentration, 30%  
Gas Velocity, 0.6 ft/sec  
Temperature, as given

Residue	Treatment	Per Cent Uranium in Bed
Rand Acid-leached	None	28.6
	Two hours at 400 C	2.8
	Two more hours at 400 C	1.7
	Two more hours at 600 C	0.7
Anaconda Carbonate-leached	None	27.0
	1½ hours at 400 C	15.1
	Two more hours at 400 C	3.6
	1.3 more hours at 500 C	0.7

## Operability and Process Improvements

Caking of solids in the reactor during a run was a problem, particularly in the early runs made at low fluidizing gas rates and low temperatures. Possibly good fluidization was not being attained in the bottom portion of the bed at the low flow rates. The lower temperature operation was complicated by the formation of  $UF_4$ - $UF_6$  intermediates. At 350 C the bed had a white color and analysis showed that a large portion was uranium pentafluoride. The pentafluoride melts at approximately 357 C. Higher flow rates and temperatures produced better operation. Except for one instance, the caking occurred on the walls of the reactor and appeared to start by forming a bridge from the central thermowell to the wall.

In general, the reactor and auxiliaries operated satisfactorily although improvements such as a reactor cooling system, a fluorine recirculating pump and a solids sampling system would be advisable in any further pilot plant studies. A cooling system for the reactor would allow operating at conditions producing uranium hexafluoride at a high rate. Faster recovery and limitation of temperature surges would also result. The fluorine recirculating pump would enable operation at a higher fluorine concentration (heat removal permitting) saving considerably on the cost of the fluorine and keeping the load on the gas scrubber-neutralization system low. The pump would not be necessary in a production plant where a high fluorine utilization is encountered and where any unreacted fluorine could be recovered by passing it through a bed of uranium tetrafluoride. The solids sampler for the reactor would be useful for determining the change in composition of a bed during a run.

The condenser operated satisfactorily at the operating conditions. Analyses of exit gas sampled showed that generally from one to two per cent of the entering uranium hexafluoride gas was not condensed. An extreme of 4.5 per cent of the gas was not condensed in a run made at a high uranium hexafluoride production rate and with a high initial loading of solid in the condenser.

Analyses of the uranium hexafluoride product indicated that the 10-micron sintered pressed powder filters were not removing all of the entrained dust from the gas. The presence of nonvolatile materials such as sodium in the product was believed due to passage of particulate material through the filters. The amount of solids trapped by the filters varied from one to four per cent of that fed into the reactor. Generally, the material was white and contained 25 to 50 per cent uranium. In future equipment it may be desirable to remove the major portion of the dust in a cyclone to reduce the number of blowbacks required on the filters.

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VI. APPENDICESAPPENDIX AMELTING AND BOILING POINTS OF SOME FLUORIDES  
ANTICIPATED IN THE FLUORINATION OF  
CRUDE URANIUM TETRAFLUORIDE

<u>Fluoride</u>	<u>Melting Point, C</u>	<u>Boiling Point, C</u>
UF <sub>6</sub>	64 <sup>a</sup>	56.4 <sup>b</sup>
VOF <sub>3</sub>	300 (?)	110 <sup>b</sup>
VF <sub>5</sub>	19.0	48.5
POF <sub>3</sub>	-40	-39
MoF <sub>6</sub>	17.5	35
BiF <sub>5</sub>	-	550 <sup>b</sup>
SbF <sub>5</sub>	7	150
CrF <sub>4</sub>	-	300 <sup>b</sup>

<sup>a</sup>Triple Point<sup>b</sup>Sublimation PointFLUORIDES WITH BOILING POINTS UNDER -40 C

PF <sub>3</sub>	SO <sub>2</sub> F <sub>2</sub>	SiF <sub>4</sub>	AsF <sub>5</sub>
PF <sub>5</sub>	SF <sub>6</sub>	BF <sub>3</sub>	

FLUORIDES WITH BOILING POINTS OVER 600 C

FeF <sub>2</sub>	VF <sub>3</sub>	NiF <sub>2</sub>	CaF <sub>2</sub>	CrF <sub>3</sub>	MgF <sub>2</sub>	AlF <sub>3</sub>
FeF <sub>3</sub>	NaF	CuF	CuF <sub>2</sub>	PbF <sub>2</sub>	PbF <sub>4</sub>	

APPENDIX BFLUORINE EFFICIENCYMethod of Calculation

Run No. 2

Feed: Rand Acid-leached Uranium Tetrafluoride

Gas Flows: Into the reactor - nitrogen 7.04 cfh at 30 C, 1 atm.

- fluorine 15.9 cfh at 30 C, 1 atm.

Purge Gas - at screw feeder 1.0 cfh

- at two pressure points 0.9 cfh

Product Uranium Hexafluoride Condensed: 2.09 lb/hr

The fluorine efficiency as defined here is

$$\begin{aligned}
 \text{F. E.} &= \frac{\text{Fluorine required to produce the uranium hexafluoride collected} \\
 &\quad \text{in the condenser, mols} \times 100}{\text{Fluorine passing through the bed, mols}} \\
 &= \frac{(\text{mols UF}_6 \text{ condensed/hr}) \times \text{oxide impurity factor} \times 100}{\text{mols F}_2 \text{/hr through bed}}
 \end{aligned}$$

The mols uranium hexafluoride condensed per hour and the mols of fluorine passed through the bed per hour are taken from the experimental data:

$$\text{Mols UF}_6 \text{ condensed/hr} = \frac{2.09 \text{ lb/hr}}{352 \text{ lb/mol}} = 0.0183 \text{ mol/hr}$$

$$\text{Mols F}_2 \text{/hr through bed} = 7.04 \text{ cfh} \times \frac{273 \text{ K}}{303 \text{ K}} \times \frac{1 \text{ mol}}{359 \text{ scf}} = 0.01765 \text{ mol/hr}$$

The oxide impurity factor is a correction factor applied because not all the uranium is present as uranium tetrafluoride. Some uranium dioxide and uranyl fluoride are present which consume fluorine at greater than a one-to-one ratio. The factor is calculated as follows:



Material	Quantity in 100 lb of Feed	Mols per 100 lb. of Feed	Mols Fluorine Required to Produce Uranium Hexafluoride
Uranium tetrafluoride	80.4	0.2560	0.2560
Uranium dioxide	3.3	0.0122	0.0366
Uranyl fluoride	4.9	0.0159	0.0318
Total	88.6	0.2841	0.3244

$$\text{Oxide Impurity Factor} = \frac{0.3244}{0.2841} = 1.14$$

Therefore

$$\text{F. E.} = (0.00594 \times 1.14) (100) / 0.01765 = 38.4\%$$

#### Gas Analysis Check on the Calculation

As defined, the fluorine efficiency can be represented as the fluorine utilization or the percentage of fluorine consumed in producing the uranium hexafluoride. Since the percentage consumed is calculated, the percentage unconsumed is known and efficiency calculations can be checked by sampling the off-gas from the reactor and analyzing the contained fluorine. Thus, results should agree with that of the efficiency calculation. Gas samples were taken from the exit of the condenser, since the analysis of the sample for fluorine would be simpler if the fluoride ion from the hydrolysis of uranium hexafluoride were not present. In addition, an exit sample also checks the amount of uranium hexafluoride in the exhaust gas, since the efficiency factor could be changed if large amounts of uranium hexafluoride were lost from the condenser.

$$\text{Expected fluorine in gas sample, per cent} = \frac{(\text{Unreacted Fluorine, cfh}) \times 100}{\text{Total Gas Flow, cfh}}$$

$$\begin{aligned} \text{Unreacted fluorine} &= (1 - \text{F.E.})(F_2 \text{ into reactor, cfh}) = (1 - 0.384)(7.04 \text{ cfh}) \\ &= 4.34 \text{ cfh} \end{aligned}$$

Total Gas Flow:

Nitrogen into reactor with fluorine	15.9 cfh
Purge nitrogen	1.9 cfh
Unreacted fluorine	4.34 cfh
	<hr/>
	22.14 cfh

Expected fluorine in gas sample, per cent =  $(4.34)(100)/22.14 = 19.6$ .

The fluorine contents of two samples taken during the run were 19.0 and 19.1 per cent. This included the contribution of fluorine ion from the contained uranium hexafluoride which was negligible. The lower than expected fluorine concentration in the gas sample is not surprising since fluorine is also consumed by other materials in the solid feed, notably water. In addition, there are errors introduced by the flow metering system and the analysis of the feed material. Consequently the check of calculated with analyzed fluorine concentration is considered reasonably good.

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