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A LABORATORY INVESTIGATION OF THE FLUORINATION OF CRUDE URANIUM TETRAFLUORIDE

by

O. Sandus and R. K. Steunenberg

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Chemical Engineering Division

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A LABORATORY INVESTIGATION OF THE FLUORINATION OF CRUDE URANIUM TETRAFLUORIDE IN A FLUIDIZED BED

O. Sandus and R. K. Steunenberg

ABSTRACT

Ore concentrates have been converted directly to crude uranium tetrafluoride by hydrogen reduction and hydrofluorination in fluidized-bed reactors. Small-scale laboratory experiments demonstrated that this process can be extended to the production of crude uranium hexafluoride through fluorination of the uranium tetrafluoride in a fluidized bed. The satisfactory temperature range for the reaction lies between 300 C and 600 C. At 450 C the fluorine utilization is between 50 and 80 per cent. With excess fluorine, over 99 per cent of the uranium is volatilized from the solid material. The fluidization characteristics of certain materials are improved by the addition of an inert solid diluent to the bed.

I. INTRODUCTION

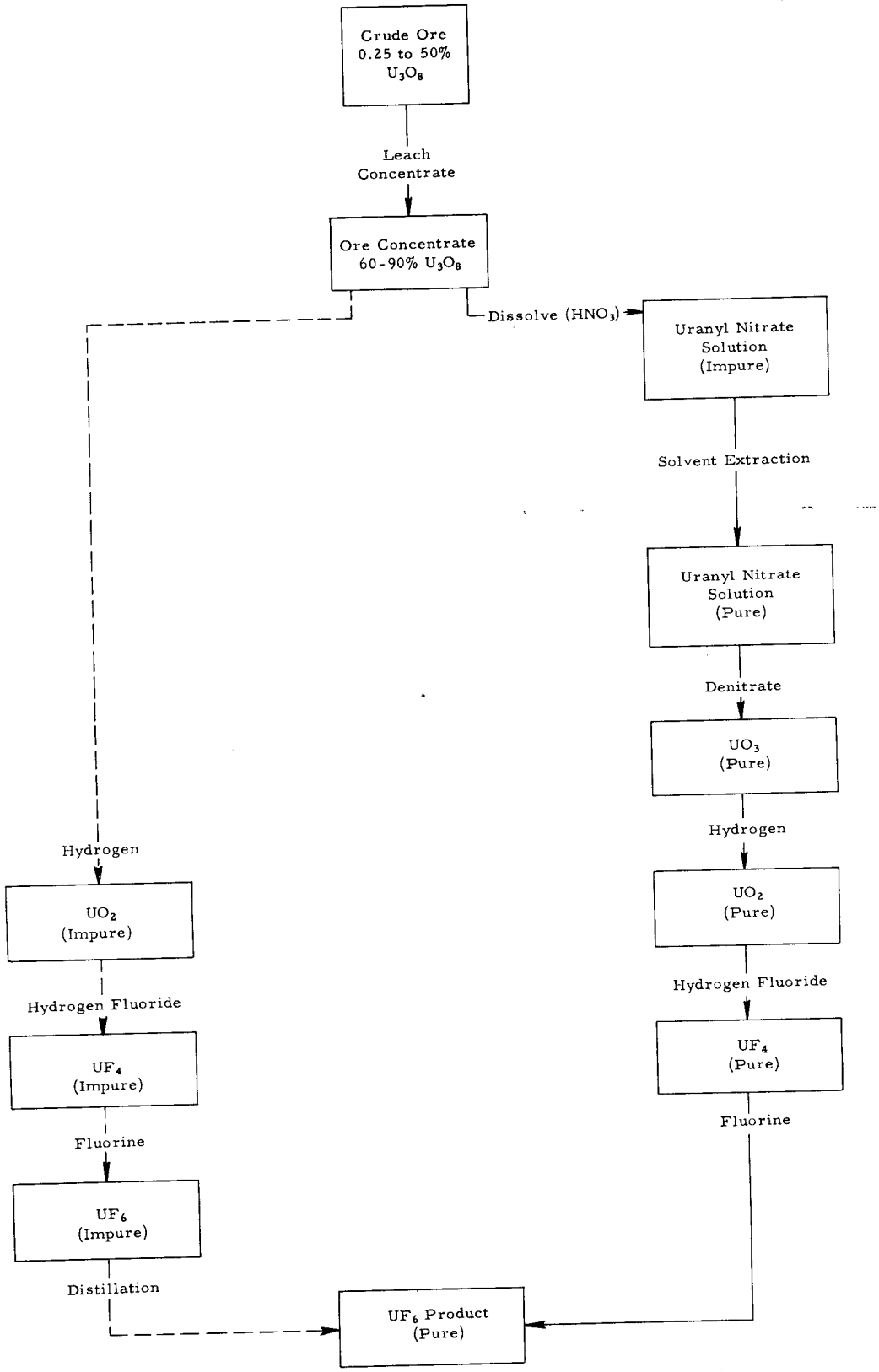
The existing process scheme for the production of specification-grade uranium hexafluoride is indicated by the solid line in Figure 1. The distillation of uranium hexafluoride affords a method for the purification of uranium which could be used instead of solvent extraction. An attractive alternative to the existing scheme might therefore be the one shown by the dotted line in Figure 1.

In this alternate, the uranium oxide in the ore concentrate is reduced to the dioxide with hydrogen, then converted to crude uranium tetrafluoride with hydrogen fluoride. Recent research on a pilot-plant scale has shown that these operations can be conducted successfully on a variety of ore concentrates in fluidized-bed reactors.[1] The use of a fluidized bed for the production of uranium hexafluoride is a logical extension of the existing technology. By this route, the solvent extraction purification and subsequent denitration steps are bypassed. Instead, the purification is accomplished by fractional distillation of the uranium hexafluoride product.

Any of several strong fluorinating agents could be used to convert the uranium tetrafluoride to the hexafluoride. Elemental fluorine is the most direct reagent in that it introduces no additional impurities into the processed material. It must be handled as a gas, which is advantageous in some respects and detrimental in others. Bromine trifluoride (bp 126 C) and bromine pentafluoride (bp 41 C) are other possibilities. Bromine trifluoride, being relatively non-volatile, is difficult to vaporize at a rate

Figure 1

ALTERNATIVE ROUTES FOR FEED MATERIALS PROCESSING



adequate for the fluidized-bed operation. The pentafluoride is somewhat more satisfactory in this respect. Both compounds have the advantage of being condensible along with the uranium hexafluoride product. Although this point may not be significant from the standpoint of collecting the product if large amounts of inert gas are used as a diluent, it is important with respect to the ease of recycling the fluorinating agent. Two distinct disadvantages are apparent in the use of the bromine fluorides. One is the cost of the bromine inventory and losses. A more important one is that the bromine specification on the uranium hexafluoride product is one ppm.[2] This separation is difficult to attain by fractional distillation. Chlorine trifluoride (bp 12 C) is another possible fluorinating agent. Its reactivity with uranium tetrafluoride (160 times faster than fluorine at 265 C)[3] may permit lower temperatures than those required by fluorine. A lower temperature is a distinct advantage for those feed materials that have low sintering temperatures. Its principal drawback is that the fluorination reaction produces chlorine monofluoride (bp 101 C) which is not condensible at reasonable temperatures.

The fluorination step has been operated in several ways. The reaction can be conducted in conventional screw or tray-type reactors.[2] It has also been carried out successfully in tower reactors, in which the uranium tetrafluoride is burned in a fluorine flame.[2] In both types of equipment, elemental fluorine was employed as the fluorinating agent, and in most cases purified uranium tetrafluoride was used.

The fluidized-bed approach should have certain advantages over these methods. It is flexible because it is well adapted to either continuous or batch-wise operation, a wide range of operating temperatures is available, and the heat of the reaction is readily removed due to the high thermal conductivity of a fluidized bed. These factors permit high throughput rates in relatively small, compact equipment. It also appears that waste gangue element fluorides can be removed conveniently with low uranium losses. The principal shortcoming of the fluidized-bed reactor for this step is that impure uranium tetrafluoride from the hydrofluorination step must possess adequate fluidizing characteristics. In some instances when difficulty was experienced in fluidizing this material, it was found that the addition of an inert, solid diluent to the bed was beneficial.

The purpose of this laboratory program was to examine in a bench-scale unit the general feasibility of fluorination in a fluidized bed. The work was limited to scouting studies on the operation in general, some of the process variables involved, and the behavior of the impurities. A detailed investigation of the optimum operating conditions was not attempted, in the belief that better results would be obtained in larger-scale equipment now under construction.

II. CHEMICAL ASPECTS OF THE FLUORINATION PROCEDURE

A. The Starting Material

1. Ore Concentrates

The material used in the experimental work was produced from three types of ore concentrate which are believed to be typical. These included Rand ore concentrate from South Africa and Anaconda acid-leach and carbonate-leach materials from domestic sources. The Rand concentrate was produced by acid leaching and an ion-exchange step, followed by precipitation of ammonium diuranate, extrusion and calcination.[4] The Anaconda acid leach material was produced by a resin-in-pulp ion-exchange process, using ammonium hydroxide as a precipitant, forming ammonium diuranate.[4] Anaconda carbonate-leach ore concentrate resulted from a carbonate leach-sodium hydroxide precipitation process which forms sodium diuranate.[4]

The uranium tetrafluoride was prepared from these ore concentrates by hydrogen reduction and treatment with hydrogen fluoride in a pilot-plant installation consisting of two multi-stage fluidized-bed reactors.[1] The various stages of the reactors used in the two steps were operated at temperatures from 300 to 600 C, and the residence time of the material was 5 to 10 hours for each of the two steps. For the purposes of this discussion the hydrogenated and hydrofluorinated product produced from ore concentrates by this procedure is designated crude uranium tetrafluoride or green salt.

2. Crude Green Salt

The mechanical properties of the crude green salt from the three sources are listed in Table 1. The principal difference among them in this respect is the low bulk density of the Rand material. Since the fluorination experiments were conducted in a small bed, the green salt used was usually screened to finer than 40 mesh particle size. The material from all three sources was reasonably free-flowing. The Rand material was fluidized easily and presented few mechanical problems. The Anaconda acid-leach material fluidized almost as easily as the Rand. The carbonate leach green salt, however, had much poorer fluidizing characteristics than the other two.

The principal impurities, mostly resulting from gangue material in the ore concentrate, are indicated roughly by the analytical data in Table 2. A significant amount of purification was accomplished by the reduction and hydrofluorination of the ore concentrate, particularly with respect to the removal of boron, silicon, ammonia, arsenic, molybdenum, antimony, and halogens other than fluoride. There are also indications that phosphorous and sulfur were removed to a large degree.

Table 1

SCREEN ANALYSES AND BULK DENSITIES OF CRUDE GREEN SALT

Crude green salt produced in pilot plant by hydrogen reduction and hydrofluorination of ore concentrates from the indicated sources.

	Anaconda Acid Leach	Anaconda Carbonate Leach	Rand South African
Bulk density (tapped), g/ml	2.7	2.7	1.6
Screen analysis, per cent			
Sieve No.			
+20	0.20	0.05	0.1
-20 +40	0.1	6.4	46.1
-40 +60	7.6	27.7	29.0
-60 +100	25.0	30.5	14.0
-100 +200	36.3	31.9	8.0
-200 +325	24.1	12.4	1.3
-325	6.8	0.9	1.5

The uranium in the crude green salt was not necessarily all in the form of the compound uranium tetrafluoride. The conversion of the oxide was not quantitative, as shown by the data in Table 3. In this case the ore concentrates had been reduced and hydrofluorinated in a fluidized bed reactor at 450 C. The amount of unconverted or partially converted material was small, but too large to tolerate as a loss. Fluorine converts this oxygen-containing material to uranium hexafluoride, however, so the problem consists only of handling small amounts of oxygen released during the fluorination.

There exists an additional problem regarding the state of the uranium in the crude green salt. A small amount of alkali-metal fluoride impurity, such as sodium fluoride, represents a substantial mole fraction, due to the relative atomic weights of sodium and uranium. For instance, the carbonate-leach material used in the experiments contained 13 weight per cent sodium fluoride, which corresponds to approximately 56 mole per cent. The melting points of sodium fluoride and uranium tetrafluoride are high -- 995 C and 1036 C, respectively. The binary phase diagram, however, shows a wide composition range with melting points between 600 C and 700 C.[5,6] This lowering of the melting point probably produces a similar lowering of the sintering temperature, which leads to difficulties in the fluidized-bed operation. It is also questionable whether the rate of fluorination is the same for the various compounds in this binary system as it is for pure uranium tetrafluoride.

Table 2

SUMMARY OF MINOR CONSTITUENTS IN CRUDE GREEN SALT

Crude green salt produced in pilot plant by hydrogen reduction and hydrofluorination of ore concentrates from the indicated sources

Element	Weight Per Cent		
	Rand Ore[a,d] Green Salt	Anaconda Acid Leach[b,e] Green Salt	Anaconda Carbonate Leach[a] Green Salt
Ag	--	0.0001	
Al	1	0.02	
As	--	0.001	
B	0.5	0.0001	0.005
Ba	--		
Be	--	0.00005	
Bi	--		
Ca	1.5	0.1	
Cd	--		
Co	--	0.0005	
Cr	--	0.001	
Cu	0.5	0.007	
Fe	0.4	0.1	
K	0.05	0.005	
Li	0.0003	0.0001	
Mg	0.04	0.1	
Mn	0.08	0.007	
Mo	--	0.002	0.1
Na	0.6	0.2[c]	7[c]
Ni	0.01	0.007	
P		0.005	
Pb	0.06	0.007	
S			0.02[c]
Sc	--		
Sb		0.0001	
Si		0.002	0.02
Sn	--	0.0005	
Sr	0.003		
Th	--		
Ti	--	0.005	
V	--	0.001	0.2
W	--		
Y	--		
Zn	--	0.005	
Zr	0.4		

[a] Estimate of Accuracy: Factor of 2

[b] Estimate of Accuracy: Order of magnitude

[c] Analyses performed by wet chemical methods. Accuracy is better than the one significant figure given.

[d] Compare Table 9, p. 19.

[e] Compare Table 10, p. 19.

Table 3

ANALYSES OF CRUDE GREEN SALT PRODUCED FROM VARIOUS ORE CONCENTRATES

Crude green salt produced by hydrogen reduction and hydrofluorination of ore concentrates in fluidized bed reactors at 450 C.

Analysis	Per Cent by Weight		
	Rand Ore	Anaconda Acid Leach	Anaconda Carbonate Leach
U Total	72	72	65
U (IV)	71	71	55
AOI[a]	3	0.6	5
WS[b]	0.7	0.8	9

[a]Ammonium oxalate insoluble. Consisted mostly of uranium oxides, except carbonate-leach material, which contained other impurities.

[b]Water soluble. Mostly uranyl fluoride, except the carbonate-leach material which contained other impurities.

B. The Fluorination Reaction

1. Stoichiometry

The gross reaction which is the basis of the fluorination step is the following:

$$UF_4 + F_2 = UF_6 \quad , \qquad (1)$$

There is evidence, however, that the reaction is more complex than the one indicated.[5,7] Three intermediate uranium-fluorine compounds have been identified - U_4F_{17}, U_2F_9, and UF_5. Thus the fluorination may be a multi-step reaction involving one or more intermediates, as explained on page 25. The intermediate compounds are formed when insufficient fluorine is present to convert all the uranium to the hexafluoride or when the uranium hexafluoride product is passed through unreacted uranium tetrafluoride. A practical problem which may result from these intermediate compounds is the possibility that they may form mixtures which melt or sinter in the fluidized bed.

2. Rate

The rate of fluorination of uranium tetrafluoride to the hexafluoride has been investigated by V. Y. Labaton,[8] who used a thermobalance in making the measurements. It was found that the reaction rate is

not detectable under 200 C and that it is dependent upon temperature. A correlation based on a continuously diminishing spherical interface for the gas-solid reaction was found to fit the rate data. The temperature dependence of the rate obeyed the Arrhenius relationship, yielding an activation energy of 19 to 20 kcal per mole. The rate of the reaction was not affected by the gas velocity, but it was proportional to the fluorine concentration. The rate was also dependent upon the area of the solid, but it could not be predicted from solid surface areas determined by gaseous adsorption.

3. Impurities

The principal impurities in crude green salt produced by the hydrogen reduction and hydrofluorination of ore concentrates are indicated in Table 2. The fluorides of those elements which may be present at this stage of the process are listed in Table 4, along with their melting and boiling points. Most of these materials are non-volatile, and they should remain in the bed during the fluorination unless they are carried out as finely divided particulate matter. In this group are certain products of the radioactive decay of natural uranium. These daughters may be sufficiently radioactive, due mostly to 24.1-day thorium-234, to require a small amount of shielding of the solid wastes resulting from the fluorination step in large-scale operations.

The volatile fluoride impurities which are collected with the uranium hexafluoride product would probably be removed by fractional distillation. Two of the principal gangue elements which form volatile fluorides are molybdenum and vanadium. Pilot-plant distillation studies (ANL-5633, page 51) have indicated that molybdenum and vanadium fluorides can be separated from uranium hexafluoride. A charge of uranium hexafluoride containing 460 ppm molybdenum and 31 ppm vanadium as the fluorides was reduced by distillation to approximately 1 ppm each. The fluorides of both molybdenum and vanadium were more volatile than uranium hexafluoride. The distillation column used in the experiments was a 16-ft, 1.75-in. ID tower filled with Heli-Pak 3019.

Volatile impurities other than gangue element fluorides may also be found in the product. For instance, small amounts of residual hydrogen fluoride from the hydrofluorination step may be present. The performance required of the distillation columns used for the final product purification will be determined by the concentrations of these volatile impurities, their volatilities relative to that of uranium hexafluoride, and the product specifications for the particular elements involved.

C. Product Specifications

The specifications for uranium hexafluoride purchased by the Atomic Energy Commission are given in Table 5.

Table 4

PROPERTIES OF GANGUE ELEMENT FLUORIDES

Element	Fluoride	Melting Point, C	Boiling Point, C
U	UF_6	64[a]	56.4[b]
V	VOF_3	--	110[b]
	VF_3	1100	1400
	VF_5	19	48
P	PF_3	-151	-101
	PF_5	- 94	- 85
	POF_3	- 40	- 39
Mo	MoF_6	17.5	35
S	SF_6	--	- 64[b]
	SO_2F_2	-137	- 55
Fe	FeF_2	1102	(1800)
	FeF_3	(1000)	(1100)
Na	NaF	995	1704
Cu	CuF	(908)	(1300)
	CuF_2	950 (decomposes)	--
Ni	NiF_2	(1000)	(1600)
Pb	PbF_2	855	1290
	PbF_4	--	500[b]
Bi	BiF_5	--	550[b]
Sb	SbF_5	7	150
As	AsF_5	- 80	- 53
B	BF_3	-127	-100
Ca	CaF_2	1418	2500
Si	SiF_4	--	- 95[b]
Al	AlF_3	--	1257[b]
Cr	CrF_3	1100	(1400)
	CrF_4	--	300[b]
Mg	MgF_2	1263	2227
Mn	MnF_2	856	--

[a]Triple Point

[b]Sublimation Point

Table 5

SPECIFICATIONS ON URANIUM HEXAFLUORIDE PRODUCT[2]

1. The uranium hexafluoride shall not contain more than 0.004 mole fraction of impurities as determined by freezing point depression.

2. The following maximum on individual elements present as volatile[a] and moderately volatile[b] compounds shall not be exceeded:

Element	Maximum (ppm by weight sample basis)
Boron	1
Bromine	1
Chlorine	100
Silicon	100
Vanadium	1
Molybdenum	1
Phosphorus	50
Chromium	25

3. The uranium hexafluoride shall be free from contamination by any hydrocarbon, partially substituted halohydrocarbons or chlorocarbons.

4. Uranium hexafluoride shall contain no detectable amounts of ruthenium, niobium, tantalum, or titanium. (Present detectable limits are Ru: 1 ppm; Nb: 3 ppm; Ta: 40 ppm; and Ti: 3 ppm.) Analytical procedures are being developed toward reducing the detectable limits on Nb, Ta, and Ti to 1 ppm.

5. The total non-volatile metal[c] impurities shall not exceed 500 ppm.

---

[a]Volatile Compound - A compound readily separated overhead by distillation, the pure material having a vapor pressure of one atmosphere at 20 C, or below.

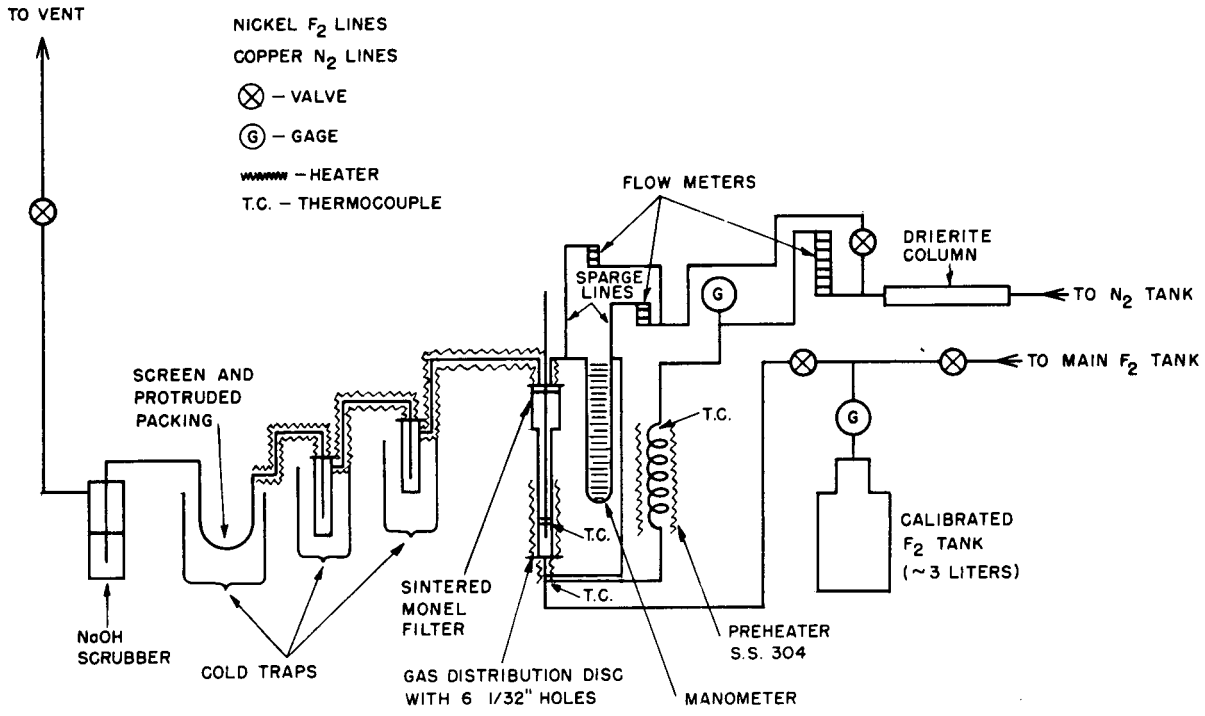
[b]Moderately Volatile Compound - A compound having a vapor pressure of one atmosphere between 20 and 300 C.

[c]Non-volatile Compound - A compound having a vapor pressure of one atmosphere at or above 300 C.

III. APPARATUS AND PRELIMINARY EXPERIMENTS

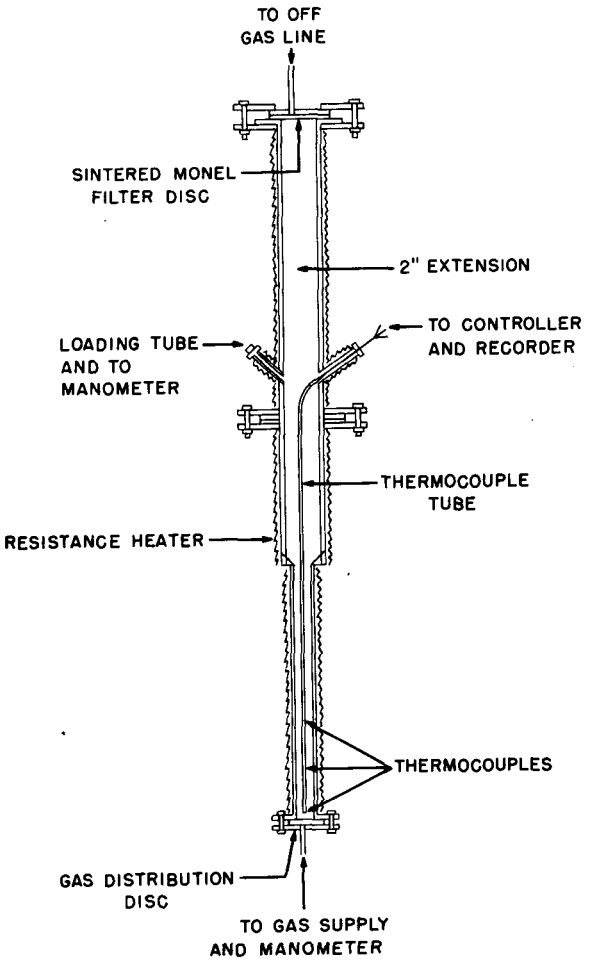
The one-inch fluidized-bed reactor shown in Figure 2 was constructed of nickel and Monel. The original version was made from one-inch nickel tubing with an extension which was two inches in diameter welded to the top.

FIGURE 2
SKETCH OF THE FLUIDIZED-BED APPARATUS



The one-inch tubing developed a crack during a temperature excursion and was replaced by a 12-inch section of 3/4-in. schedule 40 Monel pipe having an inside diameter of 0.824 in. A sintered Monel filter had been installed over the first cold trap, but it was found that fines were frequently carried overhead onto this filter where they were no longer in the reaction zone. The filter was therefore removed and installed at the top of the two-in. section of the reactor as shown in Figure 2. At the completion of the first series of temperature-dependency experiments (see Table 7), another two-in. extension was bolted on the reactor, and several other changes were made for convenience. The final form of the reactor is indicated in Figure 3.

FIGURE 3
SKETCH OF THE FLUIDIZED-BED REACTOR



In the first experiments with this apparatus, it was found that the crude uranium tetrafluoride produced in a batchwise manner from the Rand ore concentrate had a tendency to cake, due to the high percentage of fines present. The particle size of this preliminary batch of material, given in Table 6, may be compared with that in Table 1. The latter was made by a continuous process and represented a more typical material.

In order to observe the fluidization process directly, a glass column similar to the metal one in use was employed to study the behavior of various inert, solid fluorides which might serve as diluents for the crude uranium tetrafluoride. It has been suggested that an easily fluidizable diluent might reduce the caking tendency shown by the crude uranium tetrafluoride.

Sodium fluoride ground from pellets and screened to -40, +100 mesh was not satisfactory because of caking. Caking was also experienced with magnesium fluoride. Crystalline calcium fluoride, however, screened to +100 mesh and having a tapped bulk density of 1.7 g/ml, was fluidized readily. A mixture of 50 weight per cent crude uranium tetrafluoride in calcium fluoride fluidized somewhat better than did the uranium tetrafluoride alone. A mixture of 75 weight per cent calcium fluoride fluidized as easily as the calcium fluoride alone, and caking was eliminated at the gas distribution disc in the bottom of the reactor.

A preliminary fluorination run using the 75 per cent calcium fluoride mixture was made at 450 C in the metal apparatus. Twice the stoichiometric equivalent of fluorine was added. At the conclusion of the run, essentially clean calcium fluoride was recovered from the reactor, indicating practically complete conversion of the uranium tetrafluoride. The inside surface of the reactor and the distribution disc were clean.

Table 6

PARTICLE SIZE DISTRIBUTION OF CRUDE URANIUM TETRAFLUORIDE FROM RAND ORE CONCENTRATE

Source: Rand South African ore concentrate reduced and hydrofluorinated in 3-inch fluidized beds at 450 C

Method: Screen analysis

Sieve No.	Per Cent
+20	2.1
-20 +40	29.5
-40 +60	11.5
-60 +100	12.2
-100 +200	13.8
-200 +325	9.3
-325	21.6

Eight more shakedown runs were performed in order to gain experience in operating the equipment. Several operational difficulties were encountered, consisting primarily of unexplained failures of nickel tubing used in the equipment.

IV. EXPERIMENTAL RESULTS

A. Experiments with Crude Green Salt Produced from Rand Ore Concentrate by Batch Reduction and Hydrofluorination

Several experiments were performed in which an early batch of crude green salt from the Rand ore concentrate was fluorinated. The results are summarized in Table 7.

Run 10 - About 94 per cent of the uranium was collected as the hexafluoride. Two stoichiometric equivalents of fluorine were added separately, the collection traps being replaced between the additions. During the first addition the fluorine efficiency was about 50 per cent.

Run 11 - It was demonstrated that practically all the uranium was removed from the bed by the addition of excess fluorine. The stoichiometric equivalent of fluorine added initially showed an efficiency of 62 per cent. Additional fluorine, corresponding to the uranium tetrafluoride remaining in the bed, again gave 62 per cent efficiency. Excess fluorine was then passed through the bed to remove as much of the uranium as possible. About 95 per cent of the uranium was collected as the hexafluoride during the three fluorine additions.

Table 7

THE FLUORINATION OF CRUDE GREEN SALT IN A ONE-INCH FLUIDIZED BED REACTOR

Gas Stream: 0.073 g/min F_2 diluted with N_2 to give a gas flow of 1500 cc/min in the reactor.

Bed Contents: 25 weight per cent crude green salt; 75 weight per cent CaF_2 (+100 mesh).

	Initial Bed Composition			Fluorine Addition Data			
Run No.	CaF_2 (g)	Crude Green Salt[a] (g)	Bed Temp (C)	Stoichiometric Equivalents of Fluorine Added[b]	Time (min)	Fluorine Efficiency[c] (per cent)	Remarks
10A	56.2	18.8	450	1	30	50	
B			450	1	30	44	
11A	56.2	18.8	450	1	27	62	
B			450	1[d]	29	62	
C			450	Excess	-	-	95% of UF_6 collected
12	56.2	18.8	450	1/2	20	-	Filter plugged when operated at 450 C.
13A	56.2	18.8	450	1	30	67.5	
B		e	450	1	30	68.8	
C		e	450	1	30	67.5	
D		e	450	1	30	67.5	
E		e	450	1	30	65.5	
F-I		e	450	1	30	-	
14A	56.2	18.8	400	1	20	52.3	
B		e	300	1	30	45.6	
C		e	200	1	30	21.5	
D		e	150	1	30	10.3	
E		e	100	1	30	0.5	
18A	56.2	18.8	100	1	30	1.05	
B		e	150	1	30	0.4	
C		e	200	1	30	12.8	
D		e	250	1	30	49.1	
E		e	300	1	30	49.6	
F		e	250	1	30	48.6	2-inch extension added.
G-1		e	400	1	30	46.0	The reactor broke due to embrittlement. This was noticed after the G-1 experiment. G-2 repeated G-1 with a fresh bed after the reactor was repaired.
G-2			400	1	30	47.3	
I		e	450	1	30	48.4	
J		e	500	1	30	38.3	
19	56.2	18.8	500	1	30	31.5	This experiment repeated 18-J with a fresh bed.

[a] Purity 95.4 per cent.

[b] One stoichiometric equivalent of fluorine is that required for the reaction $UF_4 + F_2 = UF_6$.

[c] Fluorine efficiency is defined as $\frac{\text{moles of } UF_6 \text{ collected}}{\text{moles of } UF_4 \text{ initially present}}$ for one stoichiometric equivalent of fluorine.

[d] Based on the unreacted green salt remaining in the bed.

[e] Green salt added to restore the bed to its original composition.

Run 12 - The sintered Monel filter at the top of the reactor was heated to 450 C instead of the usual 100 C in an effort to reduce slight caking of the material on and near the filter. When half the stoichiometric equivalent of fluorine had been added, the filter became plugged, apparently by corrosion products. Since its operation at lower temperatures had been reasonably satisfactory, the filter was maintained at 100 C in the remaining experiments.

Run 13 - It was shown that the fluorination reaction in the fluidized bed could be operated on a semi-continuous basis to produce about 100 g of uranium hexafluoride. Nine cycles were carried out, each cycle representing the addition of a stoichiometric equivalent of fluorine, and the addition of enough crude uranium tetrafluoride to return the bed to its original composition. In the first cycle an average fluorine efficiency of about 67 per cent was realized, the highest obtained in any of the runs. At the end of the fifth cycle some plugging occurred in the gas distribution plate at the bottom of the bed. The minor difficulties encountered were believed to result from the design of the small laboratory-scale equipment.

Run 14 - An effort was made to gain a rough indication of the temperature dependence of the reaction. Operationally, the procedure was identical to that of Run 13, except that the temperature of the bed was varied. A strong temperature effect was shown by the fluorine efficiency, which dropped to 0.5 per cent at 100 C.

Run 18 - An additional experiment was performed in which the reactor was operated semi-continuously, the temperature being changed with each addition of uranium tetrafluoride. The operation was similar to that in Run 14, except that the temperature was changed in reverse order with the lower temperatures first, and the 2-in. extension was used. Both runs agreed in showing that the rate of fluorination below 250 C was slow. This is in agreement with the work of Labaton,[8] who found no detectable reaction rate below 220 C. In Run 14, however, the fluorine efficiency increased with temperature, while in Run 18 the fluorine efficiency was essentially constant in the 250-450 C range. The differences in the two runs may be explained, at least partially, by the work of Labaton,[7] which indicated that the fluorination rate of uranium tetrafluoride is about four times as fast as the fluorination of uranium fluorides intermediate between the tetrafluoride and the hexafluoride. In Run 14 it is believed that the fluorination was primarily that of uranium tetrafluoride until the temperature had been reduced below 250 C. In Run 18 the fluorination was probably that of the uranium intermediates which had consumed part of the fluorine in their formation. At 250 C uranium tetrafluoride began to be fluorinated along with the intermediates. The lower values at 500 C are probably due to caking, which becomes substantial

above 450 C. It is also possible that the addition of the two-inch extension may have affected the results by allowing some of the bed material to stick to the walls of the extension. The surface area of the extension walls was large compared to the amount of uranium tetrafluoride present in the bed.

B. Experiments with Crude Green Salt Produced from Rand Ore Concentrate by Continuous Reduction and Hydrofluorination

The fluorination experiments discussed in the previous section were performed with a batch of crude green salt with poor fluidization characteristics. The fluidization properties were of extreme importance in the one-in. reactor, where it was necessary to use deep beds in order to handle an adequate amount of material. The large ratio of height to diameter in the one-in. reactor tends to aggravate any fluidization difficulties.

Therefore, a second batch of crude green salt with excellent fluidization properties was used in the next series of fluorination experiments. This material, which was also produced from Rand ore concentrate, was more typical of the crude green salt produced by the fluidized-bed process. The particle size distribution of the batch is presented in Table 1. When the +40 mesh particles were removed from this material by screening, it had excellent fluidizing properties.

The results of several fluorination experiments with this material are given in Table 8. No solid diluent was needed in these runs. It was found that the fluorine concentration in the fluidizing gas stream did not affect the fluorine efficiency appreciably, but it did have a strong influence on the rate of uranium hexafluoride production.

The bed residue and the uranium hexafluoride product of Run 20 were submitted for spectrochemical analyses in order to obtain the distribution of the gangue elements. The results, given in Table 9, indicated that the uranium hexafluoride was contaminated with compounds of boron, potassium, lithium, sodium, and possibly lead, silicon, and zirconium. The reason for the presence of the non-volatile fluorides, such as those of the alkali metals, was not clear, although further work described in the next section has led to a possible explanation.

C. Experiments with Crude Green Salt Produced from Anaconda Acid Leach Ore Concentrate

A sample of crude green salt produced by the reduction and hydrofluorination of Anaconda acid-leach ore concentrate was obtained for fluorination studies. The bulk density and screen analysis of the material are given in Table 1.

Table 8

THE FLUORINATION OF CRUDE GREEN SALT (SECOND BATCH) IN A ONE-INCH FLUIDIZED BED

Charge: 75 g crude green salt (71.8% U) produced from Rand South African ore concentrate

Fluorine: 1 stoichiometric equivalent

Temperature: 450 C

Linear Flow Rate: 0.5 ft/sec

Run No.	N_2	F_2[a]	Mole Ratio F_2/N_2	Time of Run (min)	Fluorine Efficiency (per cent)[b]	Uranium Balance (per cent)
20	2665	481	0.18	30	83.3	93.6
21	2310	836	0.36	17.3	77.5	96.0
22	1825	1321	0.72	10.9	69.6[c]	96.9
23	0	3146[d]	pure F_2	4.0	80.9	97.3

[a]Orifice meter added to apparatus to measure these high flow rates.

[b]Fluorine efficiency = $\frac{\text{moles of } UF_6 \text{ collected}}{\text{moles of } UF_4 \text{ originally present}}$

[c]Operational difficulties due to a plugged filter.

[d]Difficulty in maintaining a constant flow rate.

Table 9

DISTRIBUTION OF GANGUE ELEMENTS IN THE FLUORINATION OF CRUDE GREEN SALT PRODUCED FROM RAND ORE CONCENTRATE

Source: See Run 20, Table 8

Element[a]	Crude Green Salt (75 g 71.8% U) (g)	Green Bed[b] Residue (5.7 g) (g)	White Bed[b] Residue (3.5 g) (g)	Off-Gas Filter[c] Residue (1.3 g 65.6% U) (g)	UF_6 Product (66.4 g) (g)
Ag	-	0.006	0.007	-	-
Al	0.7	0.2	0.6	0.02	0.06
B	0.4	0.03	0.04	0.006	0.8
Ba	-	0.0003	0.001	0.0001	0.006 (?)
Ca	1	0.3	0.5	0.03	-
Cr	-	0.0006	0.002	0.0001	-
Fe	0.3	0.1	0.3	0.005	-
K	0.04	0.009	0.02	0.001	0.03
Li	0.0002	0.0001	0.00003	0.0003	0.0006
Mg	0.03	0.003	0.03	0.0008	trace
Mn	0.06	0.03	0.04	0.001	0.0002 (?)
Na	0.5	0.03	0.04	0.004	0.4
Ni	0.008	0.02	0.01	0.01	-
Pb	0.05	0.009	0.004	0.0006 (?)	0.01 (?)
Sc	-	0.0002	0.0007	-	-
Si	0.02	0.0009	0.001	0.0006	0.0006
Ti	-	0.0006	-	0.004	-
Y	-	-	0.0007	-	-
Zr	0.3	0.03	0.02	0.0003	0.08

[a]Estimate of accuracy: Factor of 2 except for UF_6, where the accuracy is an order of magnitude. Elements not detected: As, Be, Bi, Cd, Co, Mo, Sn, Th, V, W, Yb.

[b]The bed residue had segregated to some extent in the reactor. Uranium content of the green bed = 61.2%; uranium content of the white bed = 34.1%.

[c]Some material had collected as a cake on the sintered Monel off-gas filter.

The crude green salt fluidized with or without calcium fluoride diluent almost as well as the -40 mesh samples from the second batch of Rand material (see Table 1).

Table 10 gives the results of Run 24, the objectives of which were to determine the gangue element behavior and to demonstrate the complete fluorination with the acid-leach green salt. In order to obtain a larger sample of bed residue than in Run 20, three successive 75-gram portions of the crude green salt were used. The percentage of uranium volatilized was approximately equivalent to that with the Rand material.

The analyses indicate, as before, the presence of several elements which form only non-volatile fluorides. In order to check on the possibility of contamination during the sample preparation and analysis, the reagents and pieces of nickel and Monel tubing were submitted for spectrochemical analysis. The results showed that the reagents and the apparatus were not introducing contaminants. Glassware was ruled out as a source of contamination, since the samples were handled only in Fluorothene, polyethylene or metals. Therefore, more accurate sodium analyses were performed by wet chemical methods in order to check the spectrochemical data. The results showed that about 60 per cent of the sodium was carried overhead into the uranium hexafluoride traps.

In all the fluorination experiments a small amount of caked powder, usually white, has been found on the 10-micron sintered Monel filter at the top of the fluidized-bed reactor. A microscopic examination of this powder revealed that the particle size was probably less than one micron. It is possible that some of the very small particles might have formed an aerosol and passed through the relatively large-pored filter, while others collected on the filter forming the cake. The particles of crude green salt contain only small amounts of the gangue element impurities. As the fluorination reaction progresses and the uranium is volatilized as the hexafluoride, it would be expected that the residual material may be very finely divided. Therefore, it was not possible to distinguish the truly volatile fluorides from the aerosols.

It was expected that the bed residues would have a higher concentration of radioactive elements than the original crude green salt, since most of the activity results from a thorium daughter of uranium which does not form a volatile fluoride. This effect was investigated by determining the specific activities of the feed and the bed residue. The results were as follows:

Crude Green Salt Feed (cpm/g)	Bed Residue (cpm/g)
$\beta = 8.9 \times 10^4$	$\beta = 4.6 \times 10^5$
$\gamma = 6.1 \times 10^3$	$\gamma = 2.7 \times 10^4$

Table 10

DISTRIBUTION OF GANGUE ELEMENTS IN THE FLUORINATION OF ANACONDA ACID LEACH ORE CONCENTRATE PRODUCED GREEN SALT

Run No. 24 - 225 g crude green salt (3 successive 75 g portions)

Temperature:	450 C 1 stoichiometric equivalent of F_2 added for each portion, then excess F_2
Total Flow Rate:	0.5 ft/sec
Mole Ratio F_2/N_2:	0.36
Time of Run:	17.3 min for each portion, then until no UF_6 produced
U Volatilized:	95.3%
U Balance:	97.9%

Element	Crude Green Salt Feed[a] (225 g 72.6% U) (g)	Bed Remains[b] (10 g 32.0% U) (g)	Material Fallen[b,d] Through Gas Distribution Disc (5.6 g 71.9% U) (g)	NaOH[b] Scrubber (g)	UF_6[a] (225 g) (g)
Ag	<0.002	0.01	-	-	0.0002
Al	0.03	1	0.06	-	0.01
As	<0.002	-	-	-	<0.002
B	<0.0002	0.0005	0.0008	-	<0.00002
Be	<0.001	-	-	-	<0.00008
Bi	<0.0002	-	-	-	<0.0002
Ca	>0.2	0.4	0.1	0.02	0.08
Co	<0.001	-	-	-	<0.0008
Cr	0.002	0.02	0.003	-	0.002
Cu	0.02	0.3	-	0.08	0.0008
Fe	>0.2	2	0.02	-	0.02
K	0.01	0.1	0.002	0.03	0.005
Li	<0.002	0.0004	<0.0001	0.004	<0.0002
Mg	>0.2	1	0.01	-	0.008
Mn	0.02	0.03	0.006	-	0.0003
Mo	<0.005	-	-	-	0.003
Na	0.5[c]	0.2[c]	0.009[c]	-	0.3[c]
Ni	0.02	0.2	-	-	0.0002
P	0.01	-	-	-	<0.008
Pb	0.02	0.008?	0.01	-	0.0003
Sb	<0.002	-	-	-	<0.0002
Si	0.003	0.003	0.004	-	0.002
Sn	0.001	-	-	-	<0.0008
Ti	<0.01	-	-	-	<0.008
Zn	<0.01	-	-	-	<0.008

[a] Estimate of accuracy: order of magnitude

[b] Estimate of accuracy: factor of 2

[c] Analyses performed by wet chemical methods. Accuracy is better than the one significant figure given.

[d] Material fallen through gas distribution disc is not included with the bed remains. If this material is included with the bed remains, then U volatilized = 93.0%.

The specific activity of the bed residue was about five times that of the crude green salt feed. Although the amount of total activity was small in this experiment, it may require special handling in a large-scale equipment.(2)

Two experiments were performed to determine the fluorine efficiency during the fluorination of the acid-leach green salt. These are described in Table 11. The present results indicated that the acid-leach green salt behaved similarly to the Rand material.

Table 11

FLUORINATION OF CRUDE ACID-LEACH GREEN SALT IN A FLUIDIZED-BED REACTOR

Total Flow Rate: 0.5 ft/sec (3146 cc/min)
Temperature: 450 C
Fluorine: 1 stoichiometric equivalent

Run No.	Wt Crude Green Salt (g)	Mole Ratio F_2/N_2	Time of Run (min)	F_2 Efficiency(%) U Volatilized Initial U	U Balance (%)	Remarks
31	68.4[a]	Pure F_2	4.3	79.1	94.5	Slight leak at bottom of one of the tubes containing UF_6. Some small black cakes present in bed remain, and some black material cemented to walls of reactor.
32	71.8	0.72	10.3	78.0	98.5	Same as above (but no leaks in tubes)

[a]Uranium content 72.6%.

D. Experiments with Crude Green Salt Produced from Anaconda Carbonate Leach Ore Concentrate

Crude green salt produced from Anaconda carbonate-leach ore concentrate by the same process was obtained for fluorination studies. The bulk density and screen analysis appear in Table 1.

The crude carbonate-leach green salt did not fluidize as well as the material from the other sources, and the addition of calcium fluoride to the bed did not improve the fluidization appreciably. A tendency was noted for the calcium fluoride to segregate from the green salt during fluidization.

In Run 25, an attempt was made to fluorinate the carbonate-leach green salt. It was necessary to screen the sample to -60 mesh in order to attain satisfactory fluidization. Very little uranium hexafluoride was produced from the 75-g charge of green salt in the reactor. When the reactor was opened, a plug of green sintered material was discovered, extending for a considerable length in the one-inch pipe. There was a sufficient amount of sodium fluoride present in the sample to complex the uranium tetrafluoride. This was confirmed by X-ray data, which showed that little, if any, free uranium tetrafluoride was present in the crude green salt.

The sodium fluoride-uranium tetrafluoride system has been investigated by Kraus,[6] who reported only the compound $NaF\text{-}UF_4$ with a melting point of about 714 C. Eutectics at 26 and 67 mole per cent uranium tetrafluoride had melting points near 600 C and 650 C, respectively. Zachariasen[9] has studied the system by X-ray diffraction techniques. In the region of 50 mole per cent uranium tetrafluoride and greater, the X-ray data essentially corroborated the thermal analysis results of Kraus. Below 50 mole per cent uranium tetrafluoride, however, the X-ray data indicated a rather complex system of compounds. In addition, compounds such as α-, β_2- and γ-$2NaF\cdot UF_4$ and $3NaF\cdot UF_4$ were identified. More recently, work at Oak Ridge National Laboratory has indicated no $NaF\cdot UF_4$, but compounds such as $5NaF\cdot 3UF_4$, $7NaF\cdot 6UF_4$ and $NaF\cdot 2UF_4$ were found in addition to $2NaF\cdot UF_4$ and $3NaF\cdot UF_4$. Some of these, however, may represent non-equilibrium states.

It appears likely that the complex compound present in the carbonate-leach green salt was $7NaF\cdot 6UF_4$. In any case, there is no doubt that some low-melting compound existed in the sample. The melting point of the crude green salt was 670 ± 15 C. The addition of sodium fluoride to the sample (to simulate the uranium tetrafluoride depletion during the fluorination) lowered the melting point to about 610 C. Spectrochemical analyses indicated the presence of about one per cent potassium in addition to the sodium. Thus, a very complicated system is involved as the uranium is fluorinated from the bed. It is known that the crude green salt sinters at about 500 C and, under some conditions, this temperature may be even lower.

Due to the sintering tendency exhibited by the carbonate-leach green salt, calcium fluoride diluent was added to the bed to improve fluidization. The results of several fluorination experiments with this material are listed in Table 12.

Run 27 - A preliminary experiment was performed to establish whether or not the uranium could be volatilized from the bed by fluorination of the carbonate-leach green salt. The high fluidizing velocity required in this experiment may have been at least partially responsible for the low percentage of uranium volatilized; it is suggested that the reactivity of the carbonate-leach green salt may be less than that of crude green salt from the other sources.

Table 12

FLUORINATION OF CRUDE CARBONATE-LEACH GREEN SALT IN A FLUIDIZED-BED REACTOR

Total Flow Rate: 0.5 ft/sec (3146 cc/min)

Temperature: 450 C

Bed Contents: 25% carbonate leach-green salt (18.8 g) + 75% CaF_2

Run No.	Mole Ratio F_2/N_2	Time (min)	F_2 Efficiency (%) $\left(\frac{\text{U Volatilized}}{\text{Initial U}}\right)$	U Volatilized with Excess F_2 (%)	U Balance (%)	Remarks (Also see text)
27	0.02 - 0.3 excess F_2 over stoichiometry	48		51.5	64.4	Preliminary experiment. Flow rate 1 ft/sec instead of the usual 0.5 ft/sec due to unfavorable particle size of the CaF_2. Some caking of material in bed.
30	0.04 1.2 stoich. equiv. F_2, then excess F_2	30 for 1st stoich. equiv. F_2,30 for excess F_2,5 for pure F_2	48.4	84.7	90.0	Preliminary experiment. One of the fluorothene tubes containing UF_6 ignited in the stream of pure F_2. Some caking of material in bed.
33	0.72 1 stoich. equiv. F_2	2.15	35.3		108.8	Large cake about the diameter of the reactor tube present in bed.
34	0.72 1 stoich. equiv. F_2	2.15	20.8		96.4	Slight caking of material in bed.
35	0.72 excess F_2	30		99.8	106.1	

Run 30 - An experiment was performed to determine the approximate fluorine efficiency and the total amount of uranium that could be volatilized. Twenty per cent excess fluorine was added in the first part of the experiment. Since the main objective of the run was to establish the total amount of uranium that could be volatilized, the fluorine efficiency was based only on the uranium hexfluoride in the cold trap and did not include that held in lines or collected in the sodium hydroxide scrubber. It is estimated, however, that the error in the fluorine efficiency should not exceed about 20 per cent of the value quoted in the table. Two other operational difficulties may have contributed minor errors in the uranium data. One of the Fluorothene tubes in the off-gas line ignited during the run, and some of the bed contents were lost through the gas distribution plate. The results do indicate, however, that better efficiencies and uranium recoveries were possible than those obtained in the previous experiments.

Runs 33-34 - The purpose of these runs was to check the fluorine efficiencies with the carbonate-leach green salt. Although caking and sintering were present, it appeared that this material was less reactive than that from the other sources.

Run 35 - It was found that a sufficiently large excess of fluorine would volatilize most of the uranium from the bed.

In general it was found that the carbonate-leach green salt was much more difficult to handle than that from the other two sources due to its low sintering temperature and apparent lack of reactivity. By using an easily fluidized inert diluent and with an optimum choice of conditions, however, it appears that it might be handled satisfactorily in a fluidized-bed fluorination.

E. Supplementary Experiments

1. Uranium Fluoride Intermediates

Attempts were made to characterize the black material found in many of the bed residues. X-ray diffraction determinations indicated only trace amounts, if any, of uranium intermediates or uranyl fluoride (their hydrolysis product) in residues from the experiments with the crude green salt produced from Rand ore concentrate. Data in the literature appear to support the view that the fluorination reaction is a two-step process:

$$2UF_4 + F_2 \rightarrow 2UF_5 \qquad (2)$$

$$2UF_5 + F_2 \rightarrow 2UF_6 \qquad (3)$$

Labaton[8] has shown that the uranium fluoride intermediates are not formed during the fluorination if the uranium hexafluoride product is removed from the system quickly. He indicates further[7] that the reaction between uranium tetrafluoride and uranium hexafluoride proceeds in the following manner:

$$7UF_4 + UF_6 \rightarrow 2UF_4F_{17} \qquad (4)$$

$$3U_4F_{17} + 2UF_6 \rightarrow 7U_2F_9 \qquad (5)$$

$$U_2F_9 + UF_6 \rightarrow 3UF_5 \qquad (6)$$

Reaction (4) is very fast. Reaction (5) is somewhat slower than (4), while (6) is still slower than (5). At low temperatures U_4F_{17} is formed. At about 100 C, there is a rapid uptake of uranium hexafluoride to form U_4F_{17}, which reacts to produce U_2F_9 after one hour. After 1000 minutes, part of the U_2F_9 shows a tendency to produce UF_5 by the formation of $UF_{4.73}$. At higher

temperatures, but less than 300 C, there is a rapid uptake of uranium hexafluoride to a composition close to U_2F_9, and after one hour it is approximately UF_5. The reactions, especially at higher temperatures, are complicated by appreciable disproportionation of the uranium fluoride intermediates.

On the basis of this information it appears that the black material in the bed residues was not produced by the fluorination of uranium tetrafluoride, but by the uranium hexafluoride product passing through the unreacted feed. Two fixed bed experiments were performed to determine the ease of formation of the intermediates.

a. A sample of crude green salt (Rand) weighing 0.81 g was exposed to a slight excess of uranium hexafluoride, assuming UF_5 to be the product. After 0.5 hour at 90 C, the excess uranium hexafluoride was distilled off under vacuum. The green material in the reactor tube turned black almost immediately upon exposure to the uranium hexafluoride, and it showed a weight gain of 0.25 g. The corresponding weight gains for the formation of UF_5, U_2F_9, and U_4F_{17} are 0.87, 0.29, and 0.12 g, respectively, Thus, the weight increase suggested the formation of U_2F_9, in agreement with the results of Labaton.[7]

b. The crude uranium tetrafluoride was exposed to excess liquid uranium hexafluoride under pressure at 90 C for about one hour. The resulting product was a mixture of black and green particles. Since some of the solid was carried over when the uranium hexafluoride was distilled off under vacuum, the weight change was not measured. The reaction of liquid uranium hexafluoride, however, appeared to be much slower than that of the vapor.

In both experiments small quantities of the solid samples were observed to turn green upon several minutes' exposure to air. The color was apparently the same as that of the starting material.

2. Fluorination of Carbonate-Leach Ore Concentrate

A fluorination experiment was attempted, using the fluidized-bed reactor, with the Anaconda Carbonate-leach ore concentrate, which probably consists largely of sodium diuranate. The conditions were as follows:

Run: 26
Charge: 75 g carbonate-leach ore concentrate
Temperature: 450 C
Gas Flow Rate: 0.5 ft/sec
Mole Ratio F_2/N_2: 0.27

The run was not completed due to melting or sintering in the bed. The reactivity of the sodium diuranate appeared to be much greater than that of uranium tetrafluoride, and the bed temperature rose from 450 C to 600 C.

3. Fixed-Bed Fluorination Experiments

Owing to the limitations of the one-inch fluidized-bed reactor, such as losses of material through the gas distribution plate, quantitative uranium balances were difficult to attain. In order to show that there were no chemical effects inherent in the system which would prevent complete volatilization of the uranium, a group of fixed-bed fluorinations were performed. The results are presented in Table 13.

With thorough fluorination practically all the uranium was volatilized from all three types of crude green salt.

Table 13

FLUORINATION OF CRUDE GREEN SALT IN A FIXED-BED REACTOR

Fluorine Flow Rate: 0.6 g/hr

Source of Crude Green Salt	Sample Weight (g)	Temp (C)	Time (hr)	U Volatilized (per cent)	U in Bed Residue (per cent)	U balance (per cent)
Rand Ore Concentrate	0.2088	500	2	101	0.03	101
Rand Ore Concentrate	0.2384	500	1	95.3	0.02	95.3
Anaconda Acid-Leach Ore Concentrate	0.1995	330	1	94.7	0.1	94.8
Anaconda Carbonate-Leach Ore Concentrate	0.2004	330	1	103	0.3	103

4. The Behavior of Vanadium

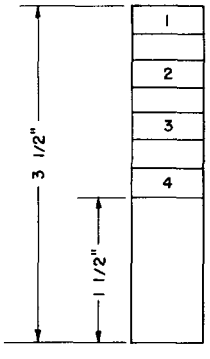
When carbonate-leach green salt samples were dissolved in nitric acid-hydrogen peroxide solutions for analysis, both the original feed material and the bed residues gave red-colored solutions. This phenomenon was not observed with the Rand or the Anaconda acid-leach material. It was known that the carbonate-leach material contained about 0.2 per cent vanadium, while the others contained practically none.

In order to determine where the vanadium appeared in the fluorination process, samples were prepared from the crude green salt feed, the uranium hexafluoride product, and the line washed before and after the cold traps. The uranium was extracted into an organic phase (20 per cent tributyl phosphate in carbon tetrachloride). The remaining aqueous phases in all the samples produced the characteristic red color when treated with nitric acid-hydrogen peroxide. This result was confirmed by spectrochemical analyses of the aqueous phases, which indicated that vanadium was the major constituent present (except for nickel in the line wash solutions).

5. Corrosion Tests*

Test specimens of "A" nickel, "L" nickel, Inconel, and Monel were identified, shaped to fit into the fluidized-bed reactor, cleaned, weighed, and inserted into the apparatus. Figure 4 indicates the locations of the specimens in the reactor.

FIGURE 4
LOCATIONS OF CORROSION SPECIMENS IN FLUIDIZED-BED REACTOR



In those experiments performed while the test specimens were present, the fluidizing gas was fluorine diluted with nitrogen, the fluorine concentration varying between 30 and 100 per cent. The fluidized bed contained crude green salt, which was diluted with calcium fluoride in some cases. The fluidizing gas velocity was 0.5 ft/sec, and the temperature was from 450 to 500 C. The total exposure during the fluorination experiments was four hours. An additional four hours of exposure to static fluorine was received during the prefluorination treatment.

Weight loss data and evaluations of the test specimens are presented in Table 14, and photo-micrographs are shown in Figure 5. The results suggest that "L" nickel and Monel should exhibit better corrosion resistance than the other two metals under these conditions. Since the

* Corrosion evaluations performed by W. B. Seefeldt and R. L. Breyne.

Table 14

CORROSION OF TEST SPECIMENS IN FLUIDIZED-BED FLUORINATION APPARATUS

Exposure: 4 hours prefluorination (static fluorine)
4 hours fluorination in fluidized bed

Temperature: 450 to 500 C

Gas Flow Rate: 0.5 ft/sec during fluorination

	Weight Loss Data			Results of Visual and Microscopic Examinations	
Specimen	Designation	Weight Loss (g)	Corrosion Rate (mils/day)[a]	Visual	Microscopic
"A" Nickel	1	0.0812	0.23	The coupon was bent while removal was being effected, but all edges looked sharp. There was a large amount of green material (UF_4) adhering to the coupon.	Metallographic examination showed intergranular attack to a maximum depth of 5 mils on the side facing the bed and 3.5 mils on the side facing the reactor tube.
Inconel	2	0.5539	1.6	The coupon looked good and had small amounts of UF_4 adhering to the surface.	Metallographic examination showed slight intergranular surface roughening with the edge facing the bed showing the greater attack.
"L" Nickel	3	0.0095	0.026	The coupon looked quite good, still possessing a lustrous finish and sharp edges. It was easiest of all coupons to clean.	Metallographic examination showed intergranular roughening of the surface on both sides with the side facing the bed showing intergranular attack. The true depth of the attack could not be determined because of the way the specimen was molded.
Monel	4	0.0158	0.044	This coupon had a film of what appeared to be copper covering the surface (possible nickel depletion). Otherwise it showed little attack.	Metallographic examination showed intergranular attack to a depth of 5 mils on the side facing the bed. The side facing the wall showed intergranular surface roughening. This section of the coupon was taken through the area of copper film.

[a]Assumed linear attack.

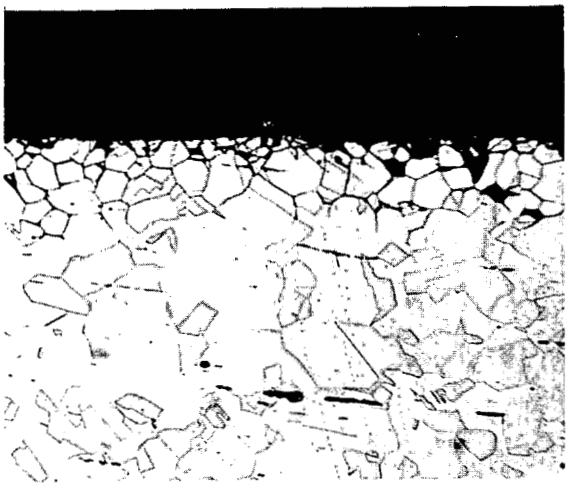
Figure 5

PHOTOMICROGRAPHS OF TEST SPECIMENS IN FLUIDIZED-BED FLUORINATION APPARATUS

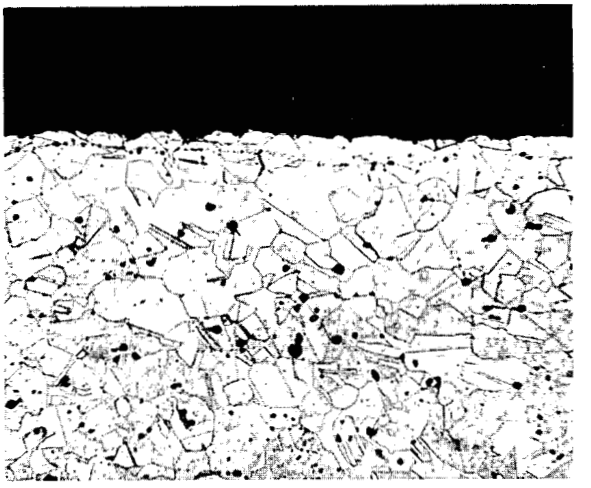
Exposure: 4 hours prefluorination (static fluorine)
4 hours fluorination in fluidized bed

Temperature: 450 to 500 C

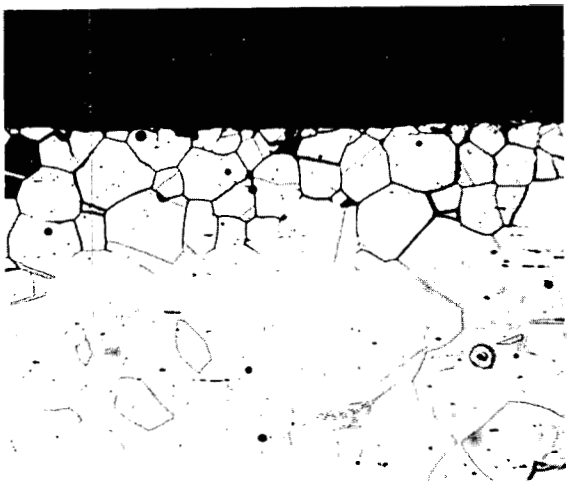
Gas Flow Rate: 0.5 ft/sec during fluidization



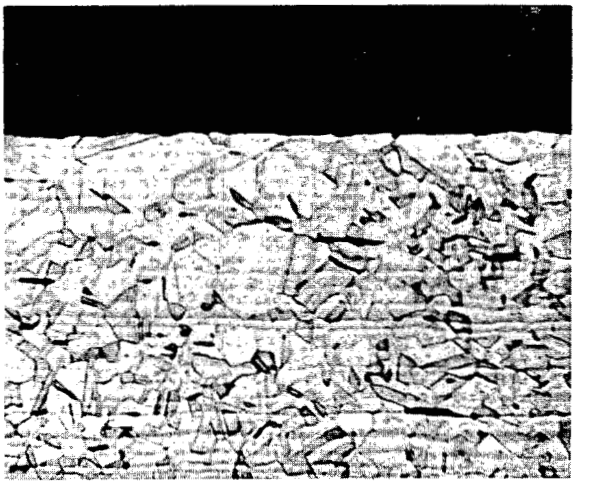
L-Nickel 100X Nitric-Acetic Etch



Inconel 100X Aqua Regia Etch



A-Nickel 100X Nitric-Acetic Etch



Monel 100X Nitric-Acetic Etch

specimen locations, temperature gradients and other variables may have influenced the results, these data should be regarded only as qualitative indications. A thorough corrosion testing program would be required in order to arrive at the best choice of a material of construction.

V. CONCLUSIONS

The laboratory experiments have demonstrated that the crude green salt can be fluorinated satisfactorily in a small-scale fluidized-bed reactor, either in a batchwise or a semi-continuous fashion. With crude green salt possessing good fluidization characteristics, the fluorine utilization was about 80 per cent for a single pass at 450 C, and it was not dependent upon the fluorine concentration over a wide range. With excess fluorine it was shown that at least 99 per cent of the uranium can be volatilized from the bed.

The satisfactory temperature range for the fluorination reaction appears to lie between about 300 and 600 C. The reaction becomes very slow at about 250 C, and above 600 C severe sintering of the crude green salt may be expected. The heat released by the fluorination reaction at 450 C is 60 kcal per mole of uranium tetrafluoride. Heat removal required no special arrangements in the laboratory experiments with the one-inch reactor, but in a larger-scale unit provisions for cooling will be necessary.

It was found that the poor fluidization properties of certain materials could be improved by the addition of easily fluidized calcium fluoride to the bed. Most of the difficulties experienced in operating the one-inch bed, especially with the carbonate-leach green salt, was probably due to the unfavorably large height-to-diameter ratio of the bed. Shallower beds should be fluidized more easily, but they would be expected to show lower fluorine utilization figures.

The uranium hexafluoride product collected in the cold traps during the fluorination runs was sufficiently contaminated to require a purification step in order to meet feed material specifications. Distillation appears to offer the best possibility for purification. Although experience is available on the distillation of halogen fluoride-uranium hexafluoride mixtures in connection with fuel reprocessing schemes, additional research is needed on the removal of gangue element fluorides from uranium hexafluoride by distillation. Other purification methods such as sublimation or fractional crystallization do not appear to be particularly promising unless distillation is found to be deficient in some respect.

The amount of useful information obtainable in the one-inch reactor was somewhat limited. Larger units, however, are not well adapted to laboratory studies, due to the large gas volumes involved and the high production rate of uranium hexafluoride product. Most of the difficulties associated with the small reactor were in achieving good fluidization of certain

materials. Those with unusually poor fluidizing characteristics may require some type of preprocessing to produce favorable particle sizes and bulk densities. Another possible solution is to blend these materials with easily fluidized feeds from other sources. In the case of the carbonate leach green salt, which was the most difficult to handle, the use of ammonium, instead of sodium, carbonate as a precipitating agent should prevent the formation of sodium diuranate and low-melting mixtures in the fluoride system.[10] It is believed that the carbonate leach-green salt can be suitable starting material if the optimum operating conditions are chosen.

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REFERENCES

1. Levitz, N. M., Petkus, E. J., Katz, H. M., and Jonke, A. A., Chem. Eng. Prog. 53, 199 (1957).

2. "Current Commission Methods for Producing UO_3, UF_4, and UF_6," TID-5295 (January, 1956)(Confidential).

3. Labaton, V. Y., "A Kinetic Study of the Fluorination of Uranium Tetrafluoride by Chlorine Trifluoride," RDB(cap)/R-8131(April, 1955).

4. Private communication, Richard L. Philippone, Met Engr, Prod. Div., AEC, Grand Junction, Colorado.

5. Katz, J. J., and Rabinowitch, E., "The Chemistry of Uranium - Part I," National Nuclear Energy Series, Vol. VIII-5, McGraw-Hill, New York (1951).

6. Kraus, C. A., "Phase Diagram of Some Complex Salts of Uranium with Halides of the Alkali and Alkaline Earth Metals," (A)M - 251 (July 1, 1943).

7. Labaton, V. Y., "Formation and Disproportionation of Intermediate Uranium Fluorides (With an Appendix on Rates of Fluorination)," IGR-R/CA-193, (October 1, 1956).

8. Labaton, V. Y., "A Kinetic Study of the Fluorination of Uranium Tetrafluoride by Fluorine," RDB(Cap.)/R-2180 (January, 1955).

9. Zachariasen, W. H., J. Am. Chem. Soc. 70, 2147 (1948).

10. Rosenbaum, J. B., Clemmer, J. B., and Lenneman, W. L., "Innovations in Processing Uranium Ores," AECU-3367 (September, 1956).