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PRODUCTION OF REFINED UF_6 FROM ORE CONCENTRATES BY FLUIDIZATION AND FRACTIONAL DISTILLATION TECHNIQUES

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INTRODUCTION

A uranium refining process based on fractional distillation of uranium hexafluoride produced by fluidization techniques offers several advantages over the existing solvent extraction process:

1. The required separation of uranium from impurities is considered to be more easily effected;
2. The uranium hexafluoride product is the desired end material if the uranium is destined for isotopic enrichment; this product can also be readily converted to uranium tetrafluoride and thence to metal;
3. The possibility of corrosion contamination is low because the purification step is the final processing operation;
4. The fluidized bed technique is superior to conventional methods for reacting gases with solids.

A process based on uranium hexafluoride distillation has become economically attractive due to technological developments which have resulted in a reduction in the cost of producing elemental fluorine(1,2) and to a greatly increased supply of high grade uranium ore concentrates assaying 70 per cent U_3O_8 or better. Despite these developments the direct fluorination of uranium ore concentrates to uranium hexafluoride without prior treatment is not considered economically feasible due to the high consumption of fluorine by gangue elements and various other impurities. To reduce

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†On loan from General Chemical Co.

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fluorine consumption it is desirable to convert the uranium and impurities to lower fluorides by reduction with hydrogen and hydrofluorination with comparatively inexpensive hydrogen fluoride. These steps have the additional advantage that a large percentage of the impurities are removed as volatile hydrides or fluorides.

A schematic flow diagram for the refining process is shown in Fig. 1. The ore concentrates first undergo a size treatment to prepare them for subsequent operations which are carried out in fluidized bed reactors. The uranium is then reduced to the tetravalent state by reaction with hydrogen at elevated temperature, then converted to crude uranium tetrafluoride, and finally to crude hexafluoride. The latter compound undergoes fractional distillation to produce the refined product. In the event that uranium metal is the desired ultimate product, the refined hexafluoride may be reacted with hydrogen to produce pure tetrafluoride, which can be converted to metal by conventional methods.

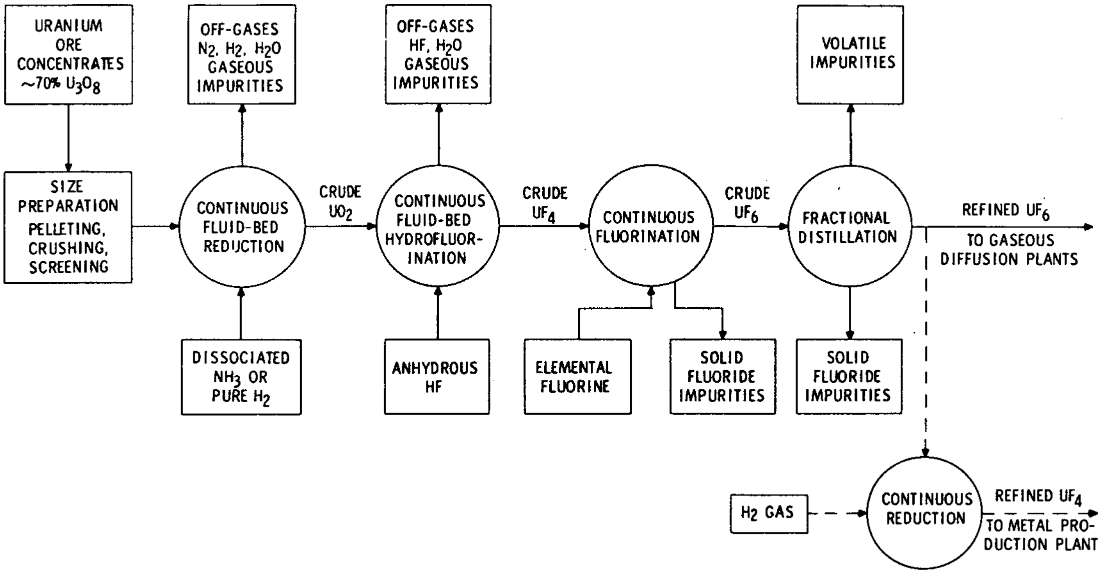

Fig. 1. Flow Diagram for Fluid-Bed Uranium Ore Refining Process

The economics and advantages of this process have been carefully weighed against other methods for uranium hexafluoride production, with the result that the fluid-bed ore refining process has been selected for use in a new uranium refinery to be completed in 1959 at Metropolis, Illinois by General Chemical Division of Allied Chemical and Dye Corporation.

Nature of the Ore Concentrates

The process used in the production of uranium ore concentrates from virgin ores varies from plant to plant depending on the nature of the uranium ore and the status of technology at the time the concentration process was installed.(3) The concentration processes are of two main types, the acid leach process and the carbonate leach process. In some plants the leaching step is preceded by a salt roast to convert the uranium to a soluble form. Ammonium and sodium hydroxides are the principal precipitants used for separation of uranium from the leachate as diuranates. The diuranates are filtered, dried and calcined to produce the final concentrates, which consist primarily of uranium oxides or diuranates (or mixtures of these) assaying at least 70% U_3O_8 in most cases. The nature and source of some of the ore concentrates studied in the development of the fluid-bed refining process are summarized in Table 1.

Table I

SOURCE AND NATURE OF URANIUM CONCENTRATES STUDIED

Source	Concentration Process	Precipitant	Nature of Ore Concentrates
South African Rand	Acid leach, ion exchange	ammonium hydroxide	Uranium trioxide and U_3O_8
Anaconda Acid Leach Plant Bluewater, New Mexico	Acid leach, ion exchange	ammonium hydroxide	Uranium trioxide, and U_3O_8
Anaconda Carbonate Leach Plant Bluewater, New Mexico	Carbonate leach	sodium hydroxide	Sodium diuranate
Vanadium Corp. of America Durango, Colorado	Salt roast, carbonate leach, fusion	-	Black oxide, indefinite composition
Union Carbide Nuclear Co. Uravan, Colorado	Salt roast, acid leach, ion exchange	ammonium hydroxide	Sodium diuranate and U_3O_8
Union Carbide Nuclear Co. Rifle, Colorado	Salt roast, acid leach	ammonium hydroxide	Sodium diuranate and U_3O_8

The physical character of these materials depends largely upon the type of drying and calcination technique used. The particle sizes range from minute crystalline powders only a few microns in diameter to large extruded pellets about 1/4-in. in diameter. For all of the concentrates a size preparation step was required before processing by fluidization methods. The coarse materials were treated by roll-crushing and screening to a size smaller than 30 mesh with the crusher adjusted to produce a minimum of fines. For the fine powders two methods of agglomeration were found to be satisfactory. The first consisted of pressing the dry powder in a standard briquetting machine into almond size briquettes, and the second consisted of dampening the powder with about 15 wt. % of water then extruding in a standard, high-capacity pelleting machine. The briquettes or air-dried pellets were then crushed and screened to size. In general the pelleting technique produced somewhat stronger particles than did dry briquetting.

In addition to physical characteristics the ore concentrates also vary widely in the type and concentration of impurities. Of the many impurities present, only sodium, molybdenum and vanadium were of major concern in the refining process. The concentration of these elements present in domestic uranium concentrates are given in Table II. Sodium enters into many of the ore concentrates from the initial salt roast step, even though ammonia is used as the final precipitant. Those materials containing the lowest concentrations of sodium and vanadium, such as the Anaconda acid-leach concentrate, are preferred for the fluid-bed process.

Table II

SODIUM, MOLYBDENUM, AND VANADIUM CONTENT OF URANIUM ORE CONCENTRATES
(Current Production of Various Mills)

Mill	Na (%)	Mo (ppm)	V (ppm)
Mines Development Co., Edgemont, S. D.	3.32	73	2,800
Anaconda (Acid Leach), Bluewater, N. M.	None	45	351
Kerr-McGee Oil Ind., Shiprock, N. M.	2.29	6500	5,100
Climax Uranium, Grand Junction, Colorado	2.07	740	16,100
Uranium Reduction, Moab, Utah	None	2700	694
Union Carbide Nuclear, Rifle, Colorado	3.29	192	9,200
Vanadium Corp. of Amer., Naturita, Colorado	6.95	<2	900
Vitre Uranium Co., Salt Lake City, Utah	5.31	4700	6,800
Vanadium Corp. of Amer., Durango, Colorado	5.07	<2	930
Anaconda (Soda Leach), Bluewater, N. M.	8.26	61	3,600
Rare Metals Corp. of Amer., Tuba City, Ariz.	None	1960	<20
National Lead Co., Monticello, Utah	None	1630	<20

Process Chemistry

The chemistry of the reduction and hydrofluorination steps is complicated by the variety of uranium compounds which can be present and by the simultaneous reaction of the reagents with impurities. The main reactions, however, are well known. Uranium trioxide, for example, reacts as follows:

$$UO_3 + H_2 \longrightarrow UO_2 + H_2O + 43{,}000 \text{ Btu/lb mol}$$
$$UO_2 + 4\ HF \rightleftharpoons UF_4 + 2\ H_2O + 82{,}000 \text{ Btu/lb mol}$$

Urano-uranic oxide (U_3O_8) reacts in a similar manner. The reactions of sodium diuranate ($Na_2U_2O_7$), product of the carbonate-leach process, have not been completely characterized, but the product obtained from the reduction and hydrofluorination of carbonate-leach concentrates has been identified by x-ray diffraction to consist primarily of the complex compound $7\ NaF \cdot 6\ UF_4$. The latter compound has a melting point at approximately 675°C whereas uranium tetrafluoride melts at 960°C.

The over-all fluorination reaction is as follows:

$$UF_4 + F_2 \longrightarrow UF_6$$

Reaction rate data, obtained with a thermobalance, indicate that this process does not proceed at any appreciable rate below 200° C. At higher temperatures, however, the rate is rapid and temperature-dependent. The temperature dependence obeys the Arrhenium relationship, yielding an activation energy of 19 to 20 kcal per mole. The rate is not affected by gas velocity, but is dependent on the fluorine concentration.

It will be shown later that a number of impurities are separated from the uranium during reduction and hydrofluorination due to the formation of volatile compounds which are carried off in the exhaust gases. Sulfate ion, a major impurity in concentrates produced by sulfuric acid leaching, is almost completely removed in the hydrogen reduction step, primarily as hydrogen sulfide. Adequate removal of sulfate in the reduction reactor is important, since sulfur is corrosive to nickel alloys used as materials of construction in the hydrofluorination step.

Another major impurity in many ore concentrates is silica. Because of its low atomic weight small amounts of silicon provide a high atomic ratio of silicon to uranium (for example, an ore concentrate having 5% by weight of silica would have an atomic ratio of silicon to uranium of about one to three). The necessity of the hydrofluorination step in the refining process is due in part to the necessity of removing silica, which would consume large amounts of elemental fluorine in any direct fluorination process. Fortunately the reaction of silica with hydrogen fluoride results in essentially its complete removal as volatile silicon tetrafluoride. Similarly boron, a neutron absorber, is separated as boron trifluoride.

Other impurities of importance in the refining process are molybdenum and vanadium, whose fluorides or oxyfluorides can be troublesome in the fractional distillation of uranium hexafluoride. It has been found that partial removal of molybdenum and vanadium occurs during hydrofluorination of some concentrates, the extent of removal depending apparently on the chemical form of the elements in the starting concentrate.

Table III lists the fluorides anticipated in the crude uranium tetrafluoride, together with their melting and boiling points. Of the fluoride impurities listed, only six are expected to contaminate the uranium hexafluoride from the fluorination reactor, assuming that the fluorination is performed at 450°C and that the uranium hexafluoride is collected in a cold trap at -60°C. The expected concentrations (based on average analytical data for ore concentrates) and boiling points of the six impurities are depicted in Fig. 2. The fluorides of phosphorus, antimony, chromium, and bismuth are expected to be present in such low concentration as to be of little consequence. Only

Table III

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
	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)	--

Element	Fluoride	Melting Point, °C	Boiling Point, °C
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

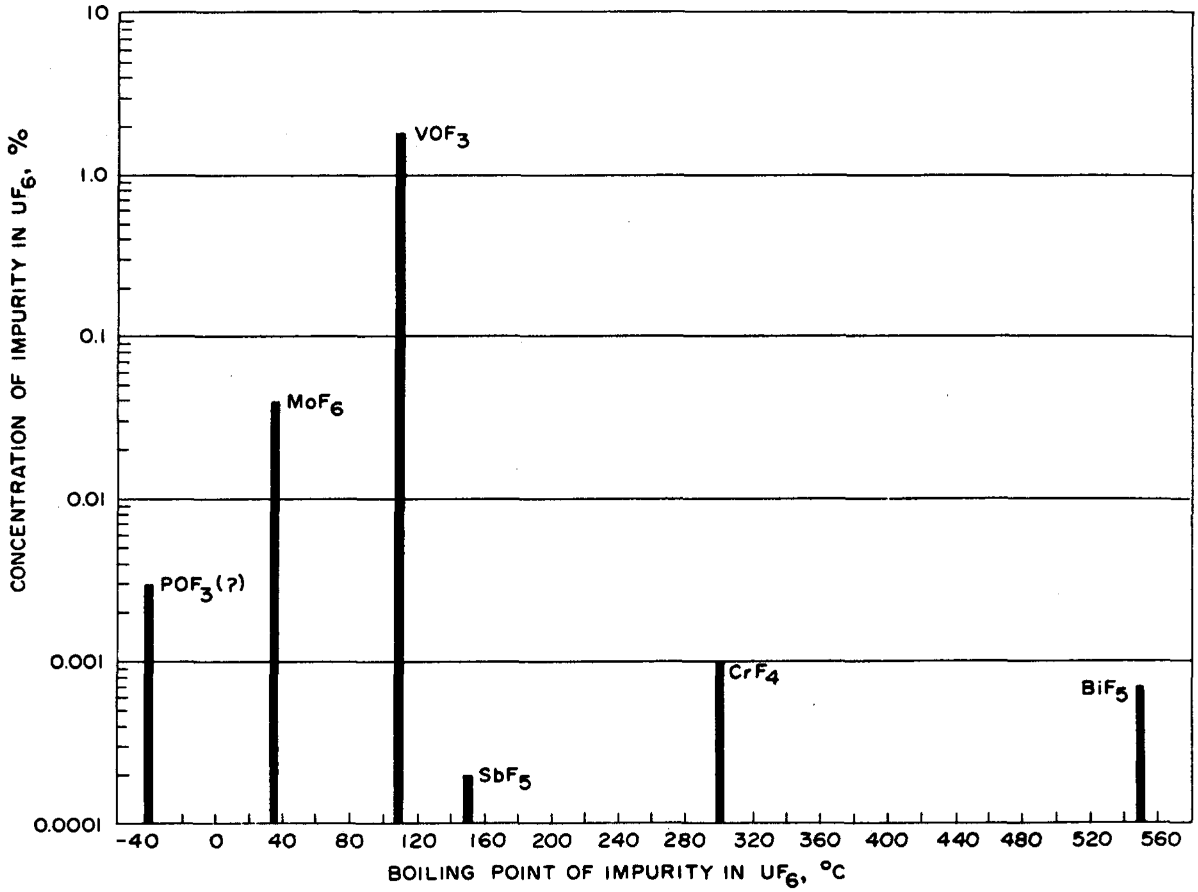

Fig. 2. Impurities Expected In Crude UF_6

the compounds MoF_6 and VOF_3 require separation by fractional distillation. It is also possible that some vanadium pentafluoride may be formed but its separation from uranium hexafluoride by distillation should not be difficult because of a favorable relative volatility of 3.2.

Choice of Gas-Solid Contacting Equipment

The types of gas-solid contacting equipment used in production plants for the conversion of refined uranium trioxide to uranium tetrafluoride include vibrating-tray reactors, horizontal screw-agitated reactors, and fluid-bed reactors. Experience with fluid-bed reactors in both pilot plants and production plants has demonstrated the superiority of this type of contactor particularly with regard to heat transfer and temperature control.(4) Since some of the hydrofluorinated ore concentrates are readily sintered at temperatures above 550° C, uniform and well controlled temperatures are a necessity. In addition the thorough and continuous agitation provided by fluidization helps to prevent caking in the bed. A disadvantage of the fluidized reactor is that pretreatment of the feed is necessary in order to provide a particle size suitable for fluidization.

In other work vibrated tray reactors were used for reduction and hydrofluorination of ore concentrates. Although these reactors performed satisfactorily on ores containing no sodium, it was not possible to process sodium-bearing concentrates without excessive sintering and caking. Similarly in the fluorination step, a tower reactor, of the type used to produce pure uranium hexafluoride from refined tetrafluoride, was not satisfactory when sodium-bearing materials were fluorinated because of caking in the high temperature zones of the reactor.

Part I

PRODUCTION OF CRUDE UF_4

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Experimental Equipment

Process development studies were carried out in fluid-bed reactors ranging in size from one to six inches in diameter. Single-stage reactors of the type shown in Fig. 3 were used for both batch and continuous runs. These units were constructed of 3-in. or 6-in. diameter pipe with an enlarged section containing filters at the top. The reactant gas after being preheated entered at the bottom and flowed upward through a porous metal gas distributor and through the bed of granular ore concentrate producing fluidization. Entrained dust particles were removed from the off-gas by two porous metal filters, one being in use while the other was being cleaned by reverse gas flow. Heat was transferred to the bed by tubular electric heaters on the outer wall, controlled by variable transformers. For continuous operation solids were metered by a feed screw into the top of the reactor, and product was periodically withdrawn from the bottom through a plug valve into a hopper. A stainless steel (type 304) reactor was employed for the reduction step and a Monel reactor for the hydrofluorination step.

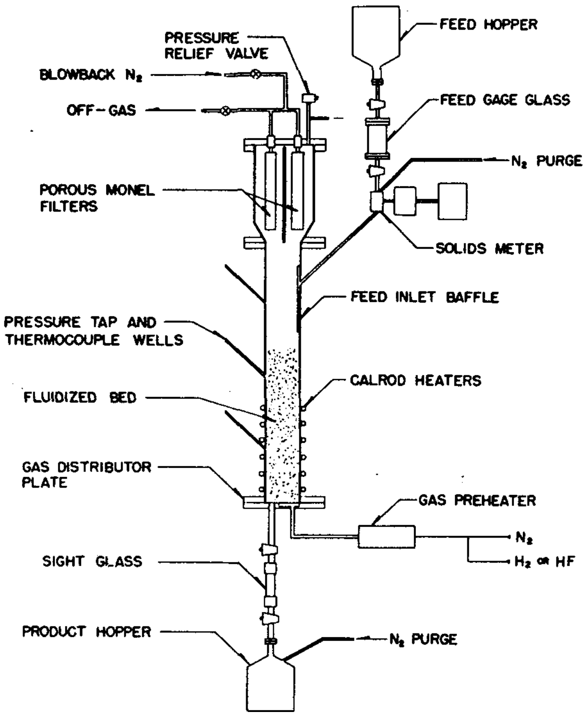

Fig. 3. Bench-Scale Fluid-bed Reactor

Additional demonstration of the process was carried out in the pilot plant shown in Fig. 4, which consisted of two multistage fluid-bed reactors together with feeder, filters, and associated equipment. The multistage reactors consisted of vertical vessels containing several fluidized beds in series, one above the other, interconnected by downcomer pipes. Granular solids were fed continuously into the top stage of the reactor and, due to the liquid-like behavior of the fluidized mass, passed downward by overflow through the downcomers from one stage to the next. Reactant gas passing upward, countercurrent to the solids flow, provided the energy for fluidization. The stainless steel reduction reactor was five inches in diameter with four stages; the Monel hydrofluorination reactor was six inches in diameter with five stages. The two reactors were operated simultaneously with continuous solids flow from the reducer to the hydrofluorinator.

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A pilot plant containing stirred fluidized-bed reactors was also operated briefly with uranium ore concentrate at the Oak Ridge Gaseous Diffusion Plant. These units contained agitators to aid in fluidization of finely powdered solids, and were intended to process ground solids rather than the more granular material used in conventional fluidized reactors.

Operating Conditions

All of the fluid-bed runs, except those made in the stirred fluid-bed reactor, employed ore concentrates which were pre-treated to a particle size range of 30 to 325 mesh. A gas velocity of 0.4 to 0.6 ft/sec was sufficient to provide moderate agitation of the solids. The reduction temperature

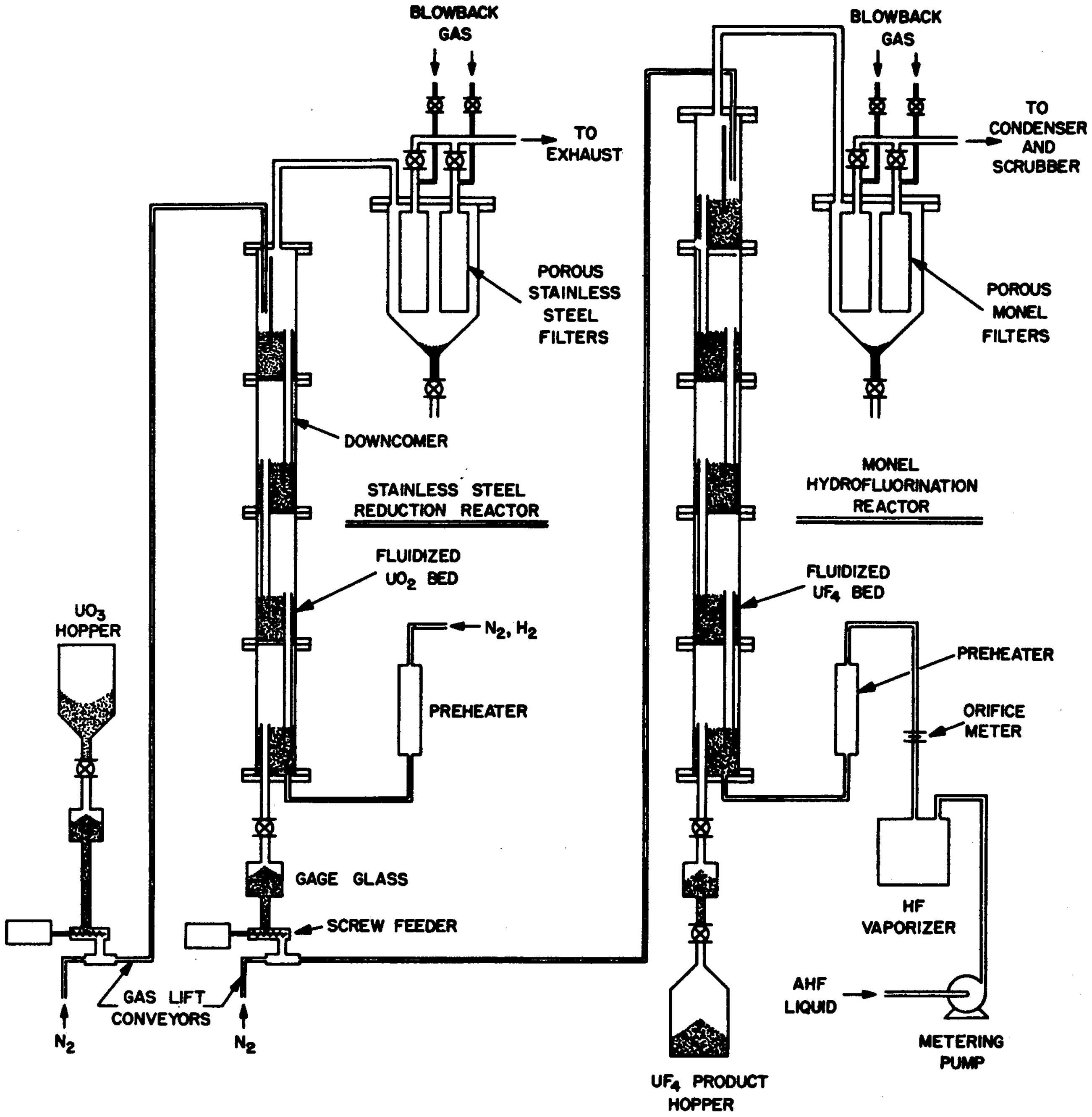

Fig. 4. Schematic Diagram of Fluidized-Bed Green Salt Pilot Plant

was 575° C, and the hydrofluorination temperature was 450° C, except where otherwise noted. The gas mixture used for reduction generally consisted of three parts hydrogen to one part nitrogen by volume to simulate dissociated ammonia, which is used as a source of hydrogen in most uranium refineries. Anhydrous hydrogen fluoride gas, containing a small amount of nitrogen purge gas, was employed for hydrofluorination.

Chemical Conversion In Single-Stage Reactors

To determine whether adequate chemical conversion could be achieved with a variety of ore concentrates, batch experiments were performed in which six different ore concentrates were hydrogen-reduced for four hr, then hydrofluorinated for another four hours. The results given in Table IV show that the reduction of uranium from the hexavalent to the tetravalent stage ranged from 82 to 98%, and the total fluoride content of the product ranged from 21 to 25%. The maximum possible fluoride content is dependent upon the impurity level, especially the sodium content. The theoretical fluoride content for pure uranium tetrafluoride is 24.2% and for the compound 7 $NaF \cdot 6\ UF_4$ (produced from sodium diuranate) is 27.0%. These batch experiments showed that all of the ore concentrates studied could be converted rapidly to crude uranium tetrafluoride without caking or other difficulties.

Table IV

SUMMARY OF BATCH FLUIDIZED REDUCTION AND HYDROFLUORINATION RUNS ON URANIUM ORE CONCENTRATES

Operating Conditions

	Reduction	Hydrofluorination
Reactor:	6-in. dia. stainless steel	3-in. dia. Monel
Bed Temperature:	575° C	450° C
Gas Composition:	50% H_2, 50% N_2	70% HF, 30% N_2
Gas Velocity:	0.4 to 0.6 ft/sec	0.4 to 0.6 ft/sec
Static Bed Depth:	6 to 21 in.	12 to 19 in.
Run Duration:	4 hr	4 hr

Ore Concentrate Source	Uranium in Feed (%)	Uranium in Product (%)	Percentage Reduction	Total Fluoride (%)
South Africa	69	73	90	23
Rifle, Colorado	66	64	98	23
Uravan, Colorado	65	72	87	25
Bluewater, N. M. (Acid leach type)	73	73	92	21
Bluewater, N. M. (carbonate leach type)	63	65	82	25
Durango, Colorado	71	66	88	24

Continuous runs were made with some ore concentrates in the same equipment. Results showed that an average residence time of at least 3.5 hr was required for the solids in the single-stage reactor to achieve 90 to 99% reduction. Results obtained in continuous hydrofluorination runs showed that these ore concentrates were exceedingly reactive toward hydrofluorination under the proper operating conditions. Average solids residence times of 2 to 4 hr were adequate for over 90% conversion at 450° C. A higher hydrofluorination temperature (550° C) resulted in greatly reduced conversion. This temperature effect is consistent with experience in the hydrofluorination of refined uranium oxides where high initial reaction temperatures were found to be detrimental to conversion due to surface sintering of the solid particles. Sintering is believed to result from the heat evolved in the reaction. The presence of sodium impurity aggravates the heat damage due to its effect in lowering the melting point of the uranium tetrafluoride.

In some of the runs the hydrogen fluoride excess was only 25 to 30% over the stoichiometric amount required for uranium and impurities. The satisfactory results obtained with these small excesses indicates that it may be feasible to neutralize the off-gas and discard the excess hydrogen fluoride rather than to attempt recovery.

In both the reduction and the hydrofluorination runs the bed remained uncaked and the product was free flowing. Only a slight reduction in particle size occurred in these operations indicating that the amount of attrition was small.

Chemical Conversion In Multistage Pilot Plant

The conditions used in the pilot-plant reactors were similar to those in the single-stage runs except that the temperatures maintained in the multiple stages of the hydrofluorinator were graded from 350° C at the top stage to 600° C at the bottom stage. A low initial reaction temperature was used to avoid sintering of the solids and to decrease the effect of the reverse reaction of water vapor with uranium tetrafluoride.

Three ore concentrates were tested in the pilot plant, two of the acid-leach type and one of the carbonate-leach type. The results are summarized in Table V. In all of the runs very high conversion to crude uranium tetrafluoride was achieved even with total residence times as low as three hr for both steps. Reduction was over 97% complete with the acid-leach concentrates and about 86% complete with the carbonate-leach material. The hydrofluorination reaction was greater than 97% complete in all runs. At the highest feed rate employed the throughput amounted to 80 lb/hr/ft^3 of reduction bed volume and 42 lb/hr/ft^3 of hydrofluorination bed volume.

Table V

SUMMARY OF PILOT PLANT RUNS ON URANIUM ORE CONCENTRATES

Reduction temperature, 575°C
Hydrofluorination temperature, 350 to 600°C

Ore Concentrate Source	Solids Feed Rate lb/hr	Average Residence Time (hr)		Run Duration (hr)	UO_2	Total U	Reduced U	Water[a] Soluble Uranium	Total Fluoride
		Reduction	Hydro-fluorination						
Bluewater, N. M. (Acid Leach)	11.0	7	10	9	1.1	72	70	0.9	25
Bluewater, N. M. (Acid Leach)	15.5	5	8	20	0.3	72	70	0.8	25
Bluewater, N. M. (Carbonate Leach)	12.6	6	7	10	3.0	65	56	9.5	24
South Africa (Acid Leach)	35.3	0.9	2.3	7	2.8	71	70	2.0	25
South Africa (Acid Leach)	24.0	1.3	3.7	7	1.7	72	71	1.5	25

[a] Water soluble uranium is a measure of the UO_2F_2 content

The analyses of stage samples taken at the end of these runs showed that the hydrofluorination was essentially completed in the first two stages of the reactor (see Table VI). This was also true for the reduction reactor in most cases. These data confirmed the conclusion reached in the single-stage experiments, which showed that the ore concentrates are highly reactive. In addition to the work already discussed, other experiments have been made on a pilot-scale in vibrating tray reactors and stirred fluidized-bed reactors. In these runs the ore concentrate was fed as received without size pretreatment. The data obtained provided additional verification that very rapid conversion of the ore concentrates to uranium tetrafluoride was possible.

Table VI

CONVERSION ACHIEVED IN EACH STAGE OF HYDROFLUORINATOR FOR VARIOUS TYPES OF ORE CONCENTRATES

Ore Concentrate Source	Feed Rate (lb/hr)	Aver. Solids Residence Time (hr)	Unconverted UO_2 (%)				
			Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Bluewater, N. M. (Acid Leach)	15.5	8	0.3	0.2	0.2	0.3	0.3
Bluewater, N. M. (Carbonate Leach)	12.6	7	13	5.4	5.2	4.2	3.9
South Africa (Acid Leach)	35.3	2.3	3.7	2.4	1.4	-	3.5

Particle Size Effects

Since some of the ores had been agglomerated and then recrushed, it was important to know whether the particles had sufficient strength to maintain their size for the duration of the processing period. Excessive production of fines was undesirable since they reduced the quality of fluidization and/or were entrained over into the filter section, requiring extra handling or reprocessing.

The sieve analyses and bulk densities of the material at various stages in the process were determined. Results showed only a slight overall decrease in size in going from the ore concentrate to the crude tetrafluoride, and only a few per cent of fines were collected in the filters in most runs. Tests in a glass column showed that the reduced and hydrofluorination products fluidized better than the feed, probably because of removal of moisture from the solids.

Purification Effected by Reduction and Hydrofluorination

In Table VII are given the chemical analyses of the ore concentrates and crude uranium tetrafluoride for certain impurities which are affected by the reduction and hydrofluorination treatment. It may be seen that about 99% of the silicon, 90% of the sulfur, and about 80% of the molybdenum were removed in the process. Arsenic and boron, present in the ore concentrate to the extent of a few hundred parts per million, were reduced to less than 10 ppm. The behavior of phosphorus and vanadium was variable depending on the ore concentrate, but in general the removal achieved for these two elements was low.

Table VII

IMPURITY REMOVAL EFFECTED BY REDUCTION AND HYDROFLUORINATION

(Hydrogen reduction at 575° C, followed by hydrofluorination at 450 to 550° C)

Ore Concentrate Source	Run Type	Status	Impurity Concentration (PPM)						
			S	As	B	Mo	P	Si	V
South Africa	Bench-scale, Continuous	Before Treatment	800	400	10	9.6	50	9,600	< 50
		After Treatment	280	<10	<1	2.0	<50	10	<20
Bluewater, N. M. (Acid Leach Type)	Pilot Plant, Continuous	Before Treatment	7,800	-	-	15	750	2,300	250
		After Treatment	70	< 10	< 1	4	< 50	15	<10
Bluewater, N. M. (Carbonate Leach)	Bench-scale, Batch	Before Treatment	600	-	2	100	600	-	5,300
		After Treatment	35	-	< 1	12	200	200	1,200
Durango, Colorado	Bench-scale, Batch	Before Treatment	7,500	-	< 1	-	130	-	-
		After Treatment	600	-	< 1	-	150	500	-
Uravan, Colorado	Bench-scale, Batch	Before Treatment	64,000	-	140	-	12,000	-	19,900
		After Treatment	600	-	< 1	-	8,000	100	10,700
Rifle, Colorado	Bench-scale, Batch	Before Treatment	24,000	-	120	300	2,000	-	16,200
		After Treatment	2,000	-	10	52	1,500	200	12,000

Other analyses showed that the sulfur was removed during the reduction operation, primarily by conversion of the sulfate to hydrogen sulfide. The removal of elements such as boron, silicon and molybdenum occurred in the hydrofluorination step by formation of volatile fluorides. Qualitative data indicated that volatile substances such as water, ammonia, carbonate, and chloride were also removed in the process. The remaining impurities were primarily elements having non-volatile fluorides such as iron, calcium and sodium, which should be readily separable in the fluorination step.

Corrosion Testing

In order to obtain preliminary corrosion data on materials of construction for the processing of uranium ore concentrates to crude green salts, metal coupons were placed in each bed of each reactor. Those tested in the reduction column were 304, 309, and 347 stainless steel. In the hydrofluorinator, Monel, Inconel, and Hastalloy B were used. After about 80 hr of exposure under process conditions one complete set of samples was removed and examined. The data indicated corrosion of the stainless steels tested was low and about equal for all types, the highest being 0.053 mil for the 304 coupon in stage 2, and the majority being below 0.030 mil for the exposure period of 80 hr. The only gross physical change noticed was a darker appearance for all the coupons in stage 1.

The coupons in the hydrofluorinator definitely showed greater corrosion in the upper stages than in the lower. This may be due to the presence of higher water concentration and/or higher gaseous impurity concentrations in these stages. Corrosion rates were low (about 0.05 mil) for all three metals in the two lowest stages (where there was little or no reaction) even though the temperatures were the highest. In the top stage Inconel and Hastalloy B (0.18 mil penetration) were definitely superior to Monel (4.1 mil).

Operability of the Fluid-Bed Reactors

The degree of trouble-free performance achieved in the fluidized-bed reactors varied with the type of equipment used and the type of ore concentrate processed. Acid-leached ore concentrates which had been size-pretreated by pelleting, crushing, and screening were processed without operating difficulties. With carbonate-leached ore concentrates, which have a high sodium content, it was necessary to use care in start-up to avoid rapid initial reaction. When the heat of reaction was not dissipated from the bed, caking resulted because of the relatively low sintering temperature of this material. However caking was encountered in the fluid-bed reactors only when hydrogen fluoride was fed too rapidly into a fresh bed of reduced ore concentrate. During continuous operation no caking or sintering was observed in either the reduction or the hydrofluorination reactors.

Some of the ore concentrates, particularly the South African material, had very low bulk density and poor flow properties. This material was difficult to feed and convey at uniform flow rates, and occasional interruptions of the runs were necessary to unblock the feed system. This difficulty was encountered only with concentrates which were received from the mill in pellet form and were reduced to size by crushing. A more satisfactory feed could be prepared by crushing these pellets to powder, then re-pelleting as was done with the other concentrates.

The single-stage fluid-bed reactors were the simplest and most trouble-free to operate. The multistage reactors operated well on feeds which had only a small percentage of fines initially, and which did not break-up into fines during processing. The multistage reactors reduced bypassing of incompletely converted solids, and therefore achieved greater conversion in a shorter residence time. However, since the residence time required for conversion of the ore concentrates was short even in the single-stage units, the additional complexity of the four-and five-stages was hardly warranted. Nevertheless the use of two-or three-stage reactors appears worthy of consideration.

The stirred fluid-bed reactors would eliminate the necessity for size-preparation of the feed, except for crushing. However, the cost of the feed preparation step is low, and the use of a mechanical stirrer introduces possible complications. In a test on acid-leached ore concentrates, the stirrer jammed on several occasions and the powder bed caked. While it is possible that this difficulty could be eliminated, satisfactory operation has not been demonstrated.

In general the performance of the fluid-bed reactors was highly acceptable, and considerably superior to other types of gas-solid reactors in general use. The flexability of the fluid-bed units for processing materials of widely varying properties was considered to be an important advantage.

Part II

FLUID-BED CONVERSION OF UF_4 TO UF_6

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Although plant-scale tower fluorinators for the conversion of highly purified uranium tetrafluoride to uranium hexafluoride already exist, this equipment may be of doubtful utility for the fluorination of crude uranium tetrafluoride. The presence of impurities, notably sodium, in the feed seriously interferes with the operation of reaction equipment which employs high conversion temperatures, as in a fluorine flame reaction. To avoid caking and sintering during fluorination, it appeared necessary to employ moderate reaction temperatures and to use equipment which would provide uniform, well controlled temperatures in the solid phase. For these reasons experiments were carried out in fluid-bed reactors.

Laboratory Experiments

Laboratory batch experiments on fluid-bed fluorination of uranium tetrafluoride were performed in a one-in. diameter Monel reactor with the necessary auxiliary equipment. All runs with the laboratory reactor were made batchwise at atmospheric pressure. The reactor was loaded with a weighed amount of uranium tetrafluoride and in some cases calcium fluoride was added as a solid diluent to improve fluidization quality and to serve as a fluidized-bed medium after most of the uranium tetrafluoride had been removed by volatilization. Nitrogen flow was started to fluidize the bed and when temperature equilibrium was attained, one stoichiometric equivalent of fluorine was passed through the bed, and the uranium hexafluoride formed was condensed and weighed. Samples of this uranium hexafluoride and the uranium tetrafluoride remaining in the bed were taken, and the bed was inspected for caking tendencies.

Samples of crude uranium tetrafluoride from the various ore concentrates were subjected to the fluorination treatment, and performance was evaluated by determining the fluorine efficiencies of the reaction defined as follows:

$$F_2 \text{ efficiency} = \frac{\text{g U in } UF_6 \text{ Produced}}{\text{g U in Fluidized Bed Originally}}$$

Data in Table VIII show that with crude acid-leached uranium tetrafluoride diluted with calcium fluoride, fluorine efficiencies of approximately 68% were obtained at 450° C with 76% fluorine in nitrogen. The effect of temperature on the reaction is also shown, and as expected the fluorine efficiency was low under 200° C. The crude uranium tetrafluoride alone without the calcium fluoride diluent gave slightly higher fluorine efficiencies than the dilute bed. The effect of fluorine concentration on the efficiency appeared to be minor.

Crude uranium tetrafluoride from acid-leached ore was processed without difficulty. Material derived from carbonate-leach ore was the most difficult to process because of sintering and caking difficulties. The melting point of this crude tetrafluoride is about 670° C. Addition of sodium fluoride to the sample (to simulate uranium tetrafluoride depletion during the fluorination) lowered the melting point to about 610° C. The use of calcium fluoride to dilute the bed, and nitrogen to dilute the fluorine, reduced caking with this material.

Table VIII

FLUORINE EFFICIENCY DATA FOR FLUORINATING URANIUM TETRAFLUORIDE IN A ONE-INCH FLUIDIZED BED REACTOR[a]

(Gas Velocity: 0.5ft/sec)

Crude UF_4 Source	Run No.	Bed Composition		Bed Temp.,(°C)	Time of Addition,(min)	F_2 Conc., (%)	Fluorine Efficiency[b]
		CaF (g)	UF_4 (g)				
South African (Acid-Leach)	1 A	56.2	18.8	450	30	7.6	68
	B		(d)	450	30	7.6	68
	C		(d)	450	30	7.6	68
South African (Acid-Leach)	2 A	56.2	18.8	400	30	7.1	52
	B		(d)	300	30	6.0	46
	C		(d)	200	30	5.0	22
	D		(d)	150	30	4.4	10
	E		(d)	100	30	3.9	1
South African (Acid-Leach)	3	None	75	450	30	15	83
	4	None	75	450	17.3	27	77
	5	None	75	450	10.9	42	70[c]
	6	None	75	450	4.0	100	81
Bluewater, N. M. (Acid-Leach)	7	None	68.4	450	4.3	100	79
	8	None	71.8	450	10.3	42	78
Bluewater, N. M. (Carbonate-Leach)	9	56.2	18.8	450	2.1	72	21
	10	56.2	18.8	450	30	42	e

[a] One stoichiometric equivalent of fluorine was passed through the bed in each run or part of run except Run 10 in which an excess of fluorine was added.

[b] F_2 efficiency = $\frac{\text{gU in } UF_6 \text{ Produced}}{\text{gU in Original Bed}}$

[c] Operational difficulties due to plugged filter.

[d] Enough green salt was added to replace the uranium volatilized in previous run.

[e] Run 10 was made to show that 99.8% of uranium could be volatilized.

Pilot-Plant Experiments

Continuous pilot-plant experiments were performed in the equipment shown in Fig. 5. The single-stage reactor was $2\frac{1}{2}$ in. in diameter, topped by a six-inch diameter disengaging section. Heat was supplied by clamshell Nichrome wire heaters, but no cooling was provided except natural convection and radiation. Uranium tetrafluoride was fed into the reactor by a variable speed screw feeder. The gas passed through sintered Monel filters (10-micron pore) and into the condenser. The 10-ft long, three-in. diameter condenser was fitted with a finned tube through which trichloroethylene was circulated from a refrigeration system. The trichloroethylene could be heated by a steam heat exchanger when it became necessary to remove the uranium hexafluoride by vaporizing it from the condenser. The condenser was placed on a weigh scale to determine uranium hexafluoride production rates.

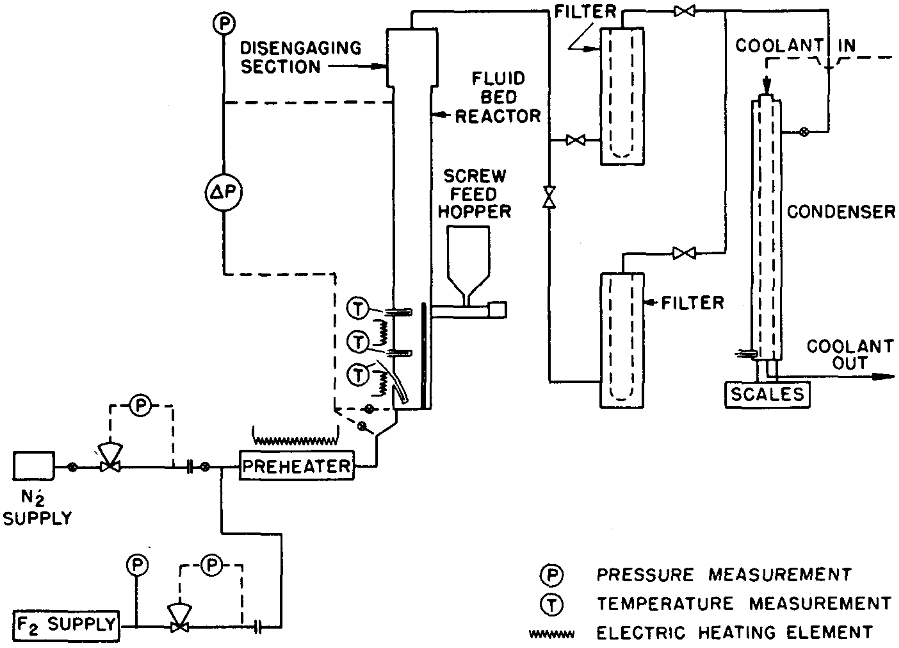

Fig. 5. Fluid Bed Fluorinator System (2.5 in. diameter)

All runs made in the pilot plant used continuous uranium tetrafluoride feed. Performance was evaluated by fluorine efficiency studies on two types of materials, refined uranium tetrafluoride and crude tetrafluoride derived from acid-leached, ammonia-precipitated ore concentrate. With the refined material the effect of operating variables such as bed height, fluorine concentration, fluidization gas velocity, temperature and bed diluent was determined.

Data in Fig. 6 show that the fluorine efficiency increased markedly with increasing temperature, but was relatively unaffected by fluorine concentrations up to 30%. With 43% fluorine in nitrogen at 400° C, the reaction rate was too rapid for the heat of reaction to be removed by natural convection and radiation in this reactor.

The ratio of fluidized-bed height to diameter was 5 to 1 in most of the experiments. Decreasing the bed height reduced the fluorine efficiency markedly as shown in Table IX. The velocity of the fluidizing gas had only a minor effect on fluorine efficiency.

The addition of inert diluent, calcium fluoride, to the bed decreased fluorine efficiency by approximately one half when either 50 or 85% inert diluent was used. The efficiency obtained when crude uranium tetrafluoride from acid-leached concentrate was processed with 85% added solid diluent, was comparable to that of the refined salt.

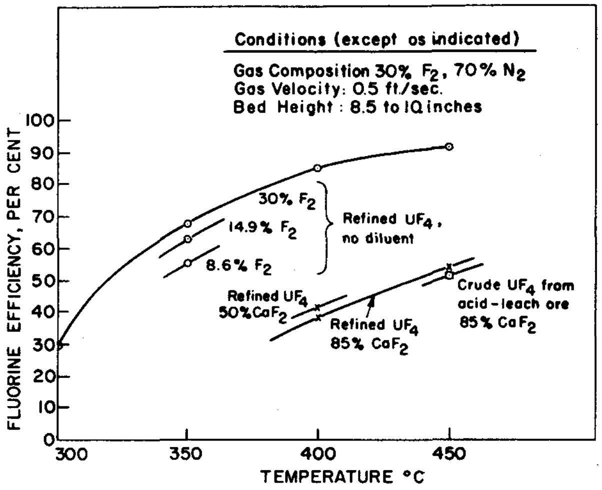

Fig. 6. Effect of Fluorine Concentration, Temperature and Bed Diluent on Fluorine Efficiency.

Table IX

EFFECT OF BED HEIGHT AND GAS VELOCITY ON FLUORINE EFFICIENCY

(30% fluorine in nitrogen)

Bed Height / Bed Diameter	Gas Velocity (ft/sec)	Temp (° C)	Fluorine Efficiency (%)
2.0	0.5	350	14
3.2	0.5	350	36
4.3	0.5	350	68
5.4	0.5	350	80
4.5	0.34	400	85
4.5	0.42	400	77 [a]
4.5	0.53	400	86

[a] Some sintering occurred in this run.

Stirred Fluid-Bed Reactor

A preliminary experiment on the fluorination of crude tetrafluoride derived from carbonate-leached ore was carried out in a 6-in. diameter, single-stage, stirred fluid-bed unit at the Oak Ridge Gaseous Diffusion Plant. The feed material was pulverized and mixed with a solid diluent consisting of minus 200-mesh magnesium fluoride slag. The starting mixture contained 7.0% sodium, and 23.9% uranium.

The initial test was made with a solids feed rate of 15.4 lb/hr, a wall temperature of 500° C, a fluorine concentration of 85%, and a superficial gas velocity of 0.1 ft/sec. No operating difficulties were encountered during the run and the solids discharged from the reactor contained only 1.8% uranium.

Tower Fluorinator

In existing production plants refined uranium tetrafluoride is converted to uranium hexafluoride in tower reactors in which powdered tetrafluoride fed into the top of the reactor is burned in a fluorine flame. Experimental runs with crude uranium tetrafluoride were carried out in a pilot-scale, four-in. diameter tower reactor. Using hydrofluorinated product derived from acid-leached, ammonia-precipitated, ore concentrate containing essentially no sodium, fluorination was performed easily in the tower reactor. The unit was operated for 22 hr with a wall temperature of 480° C, a feed rate of 43.3 lb/hr, a fluorine excess of 126%, and a fluorine concentration of 90% to produce 1,095 lb. of uranium hexafluoride. No caking was encountered and the conversion to uranium hexafluoride averaged 96.7%.

Fluorination of hydrofluorinated material derived from carbonate-leached ore was also attempted, but severe and rapid slagging occurred. Most of the slag was a yellow-white solid containing 6 to 25% sodium which apparently deposited on the walls while in a molten condition.

Purity of the Uranium Hexafluoride

Results of some analyses on crude uranium hexafluoride produced from ore concentrates are given in Tables X and XI, together with the analyses of the starting ore and the crude uranium tetrafluoride. Most of the metallic impurities were removed in the fluorination step, but all of the molybdenum and part of the vanadium remained in the uranium hexafluoride product. The concentrations of the vanadium and molybdenum will require fractional distillation of the crude uranium hexafluoride. Purification of the product by distillation is discussed in Part III.

Table X

SPECTROGRAPHIC ANALYSES OF SAMPLES FROM CARBONATE-LEACHED ORE FLUORINATION RUNS

	Ore Concentrate (%)	Hydrofluorinated Product (%)	Uranium Hexafluoride
Ca	0.30	0.03	3 ppm
Cu	0.003	NF	7 ppm
Mg	0.06	0.10	0.5 ppm
Mn	NF	0.10	0.5 ppm
Na	7.7	6.7	7 ppm
Ni	0.30	0.05	6 ppm
Si	0.80	0.5	2 ppm
V	0.2	0.4	100 ppm

Table XI

CHEMICAL ANALYSES OF SAMPLES FROM ORE FLUORINATION RUNS

Material	Mo, ppm	V, ppm
Carbonate-Leached Ore	3.0	2300
Crude UF_4	2.3	2000
Crude UF_6	3.5	<30
Acid-Leach Ore	25	250
Crude UF_6	20	25

Part III

PRODUCT PURIFICATION BY DISTILLATION

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In the process under consideration, fluorides of vanadium and molybdenum are the only impurities known to be present in the crude uranium hexafluoride, whose volatilities are such that separation by fractional distillation is required. Experimental work was carried out to determine vapor pressure data, solubilities in UF_6, and vapor-liquid equilibria for these impurity fluorides. Distillation experiments were also performed.

Vapor Pressures of VF_5 and VOF_3(5,6)

Very little information was available in the literature on the vapor pressures of vanadium pentafluoride and vanadium oxytrifluoride; and qualitative evidence suggested that the literature-reported boiling points for these compounds were considerably in error. Therefore samples of the pure compounds were prepared and identified by chemical analysis and by vapor density determinations. The vapor pressures of the solid vanadium oxytrifluoride and the liquid vanadium pentafluoride were measured as a function of temperature. These data together with the literature data for molybdenum hexafluoride and the known vapor pressure curve for uranium hexafluoride are presented in Fig. 7.

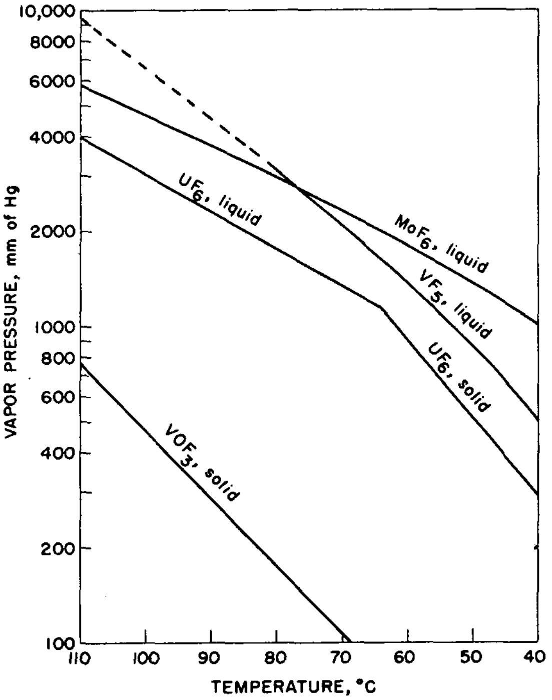


Fig. 7. Vapor Pressures of Some Fluorides of Interest to the Process

Liquid-Vapor Equilibria(7)

For proper design of the UF_6 distillation column, it was necessary to determine the liquid-vapor equilibrium relations for the major impurities expected in the crude UF_6. Since ideal solution behavior could not be assumed, vapor pressure data alone were not sufficient. Studies were carried out at the General Chemical Division, Allied Chemical and Dye Corporation with the systems MoF_6-UF_6, VF_5-UF_6, and VOF_3-UF_6.

An all-Monel apparatus consisting of a cylindrical static equilibrium chamber fitted with sampling valves was used. The apparatus was charged with the required amounts of pure UF_6 and the desired impurity, thermostatted at 75° C until vapor-liquid equilibrium was established, and samples withdrawn.

With the binary system MoF_6-UF_6 analyses of the vapor and liquid phases showed that the molybdenum was enriched in the vapor phase by a factor of 1.7 at 75° C. The enrichment calculated from vapor pressure data by Raoult's Law was 1.6 Therefore, at these dilutions, a solution of MoF_6 in UF_6 can be considered to behave ideally for engineering purposes.

With the system VOF_3-UF_6, the vanadium was found to be enriched in the vapor phase by a factor of 3.3 at 75° C. Vanadium oxytrifluoride is normally a solid at this temperature with a sublimation pressure of 135 mm of mercury, and would therefore be expected to be less volatile than UF_6. The reason for the vapor phase enrichment found in this experiment is not known at present.

In the study of the system VF_5-UF_6 the vapor phase was found to be enriched in vanadium by a factor of 3.2 whereas the ideal enrichment factor is computed to be only 1.6. From conductivity measurements it is believed that molecular association occurs in pure liquid VF_5. However, in dilute solutions in UF_6, the VF_5 would be expected to be unassociated. Consequently, the partial vapor pressure of VF_5 from such an unassociated solution would be higher (and, therefore, the enrichment factor would be higher) than that calculated using the vapor pressure of the pure but associated VF_5.

Solubilities of Impurity Fluorides in UF_6

It was important to know whether the solubilities of several fluoride impurities in UF_6 were high enough to avoid precipitation problems during fractional distillation. Solubilities were measured by distilling weighed amounts of pure UF_6 and the desired solute into Fluorothene tubes, thermostatting at 70° C, and examining the contents. The solubilities of vanadium pentafluoride, molybdenum hexafluoride, tungsten hexafluoride, and antimony pentafluoride were found to be high (greater than 10 wt. % at 70° C). The solubility of vanadium oxytrifluoride was determined in several different ways, with results ranging from 0.6 to 0.8 wt. %. The best value is believed to be 0.7 wt. % at 70° C. Since some uranium ore concentrates contain as much as 1.6% vanadium (see Table II), it was evident that the possibility of VOF_3 precipitation during distillation must be considered.

Separation of Vanadium from UF_6(7)

Since the solubility of VF_5 in UF_6 is high while that of VOF_3 is low, it was important to know which species of vanadium was present in crude UF_6. This was determined by infra-red spectroscopy. The infra-red spectra were determined by General Chemical for VF_5, VOF_3, pure UF_6, and crude UF_6. Examination of the curves showed that the main impurity present in the crude UF_6 was VOF_3.

In view of the low solubility of VOF_3 in UF_6 at 75° C and of the approximately 3:1 vapor to liquid enrichment ratio, it was necessary to examine the behavior of VOF_3 in a still column to determine whether solid VOF_3 would separate out on the fractionating plates. This problem was studied at the General Chemical Development Laboratories. For this purpose an all-glass still was constructed, consisting of a 500 ml pot, a still column containing three perforated plates, and a reflux condenser. The still assembly was placed in an air thermostat kept at 75° C. Extensive drying of the glass still was required to prevent hydrolysis of the UF_6 and etching of the glass.

The still was charged with 284 grams of a UF_6 solution containing 0.5 wt.% of VOF_3. At the beginning of the run, the UF_6 solution in the still was clear with a slight yellow cast. Reflux was initiated with the condenser temperature at 68 to 70° C, and continued for about $2\frac{1}{2}$ hr at a pressure of 20 to 24 psig. No solid particles were visible on the still plates or in the still pot, but during the run crystals began to form on the wall at the top of the reflux condenser. At the end of the run analyses of this material showed it contained 33% vanadium (80% VOF_3) and 6% uranium (9% UF_6). The observations made in this run indicated that the low solubility of VOF_3 in UF_6 would not interfere with perforate plate operation in a distillation column, but that provision for the removal of solid VOF_3 from the overhead condenser would be required.

Preliminary Pilot Plant Distillation Studies

Additional batch tests of the purification of uranium hexafluoride by fractional distillation were made in a two-in. diameter, 16-ft long packed column. The nickel column consisted of a still pot, tower, condenser, overhead receiver and associated charging and sampling facilities.

In the first run the base charge was 105 lb of previously purified uranium hexafluoride. To this was added molybdenum hexafluoride sufficient to make a still pot charge of 55 ppm molybdenum by weight. This mixture was held at total reflux for 25.5 hr under the following conditions: pressure, 45 psig; temperature, 90° C; boil-up, 46 lb uranium hexafluoride/hr. The results of samples taken during the run showed separation factors for molybdenum ranging from 160 to 1100, and the HETP was estimated to be less than two feet.

In a second run the still pot charge was made of material remaining from the previous run together with new additions of molybdenum and vanadium fluorides equivalent to 360 ppm molybdenum and 54 ppm vanadium. A boil-up rate of 35 lb UF_6/hr was used. The process operations in this run consisted of two fore-cuts followed by an overhead product cut. The process steps and corresponding sample determinations are shown in Table XII. Both molybdenum hexafluoride and vanadium pentafluoride were concentrated at the top of the column and removed in the fore-cut, resulting in subsequent collection of a uranium hexafluoride product of high purity.

Table XII

FRACTIONATION OF A MoF_6-VF_5-UF_6 MIXTURE

Phase of Operation	Amount in Fraction, lb.	Stream Sampled	Impurity Content, ppm	
			Mo	V
Charge	105.4	Still pot liquid	460	31
Total reflux (after 24 hr)		Overhead vapor	7500	136
		Bottom vapor	260	41
Forecut 1 (30/1 reflux ratio)	5.1	Distillate vapor	144	7
Forecut 2 (column holdup)	8.2	Distillate liquid	337	45
Total reflux (after 24 hr)		Overhead vapor	244	42
Product cut (10/1 reflux ratio)	60.4	Distillate liquid	1.4	<1
Column residue	4.2	Still pot liquid	7	10

Purification of Crude UF_6

Crude uranium hexafluoride prepared from ore concentrate was subjected to batch distillation at the Oak Ridge Gaseous Diffusion Plant in a 2-in. diameter column packed to a height of approximately 8 ft with Cannon protruded nickel packing. The stillpot had a capacity of approximately 125 lb of UF_6. Studies were performed with a boil-up rate of about 5300 $lb/hr/ft^2$ and a reflux ratio of 90 to 1. The concentrations of both vanadium and molybdenum were easily decreased from 27 and 18 ppm, respectively, to approximately 2 ppm. Attempts to reduce these concentrations further were not successful in initial runs.

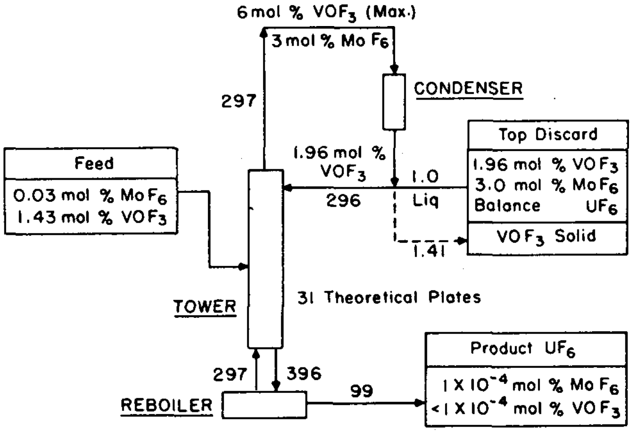
The presence of compounds of vanadium and molybdenum which are both more and less volatile than UF_6 was suggested by the fact that the concentrations of these impurities in the stillpot decreased first and then gradually increased as successive product cuts were removed.

Other experiments were carried out by General Chemical Division. Purified UF_6' was obtained from crude UF_6 by a modified distillation procedure involving selectively condensing, solidifying and separating solid VOF_3 from the vapor.

Outline of a Distillation Scheme for UF_6 Purification

The required purity of uranium hexafluoride product depends on its subsequent use. However, only very pure material is suitable as feed material for the isotope separation process. An outline is given below of a distillation scheme for the final purification of uranium hexafluoride from molybdenum and vanadium fluorides.

The basic scheme for separation of uranium hexafluoride product from these more volatile contaminants is shown in Fig. 8. In this scheme it is assumed that preceding vaporization of uranium hexafluoride has eliminated all contaminants of low volatility in the column feed. However, further purification with respect to these contaminants could be achieved by employing vapor feed to the tower or vapor take-off of the bottom product. Product is removed from the bottom, since the product is of lower volatility than the contaminants.



Relative Stream Quantities are Shown in Moles

Fig. 8. Flow Diagram of Purification Column

A special condition arises because of the limited solubility (0.7 wt.%) of vanadium oxytrifluoride in uranium hexafluoride. Concentration of impurities at the top of the column will lead to the precipitation of solid vanadium oxytrifluoride in the condenser. A suitable means is required for accommodating this solid in the condenser system and for its removal from the system. Depending on the manner of deposition of the vanadium oxytrifluoride solid, a filter may be used for removal or the solid vaporized from the condenser system with periodic purges. For continuous column operation, the latter system requires a dual condenser. (The purge method is being tested in pilot plant operations by General Chemical Division, Allied Chemical and Dye Corporation.) The uranium hexafluoride liquid condensate from the condenser furnishes the column reflux as usual. As far as the vanadium oxytrifluoride separation alone is concerned, it is possible with a solid-liquid separation to remove only the pure contaminant and recycle all the uranium hexafluoride in the liquid phase.

The other contaminant, molybdenum hexafluoride, is very soluble in liquid uranium hexafluoride and is concentrated at the top of the tower. The degree of concentration depends on the relative amount of uranium hexafluoride removed in the top impurity stream. Higher concentrations require a larger number of plates to maintain purity of the bottom product.

Because uranium hexafluoride has a triple point at 64° C and 22 psia, the distillation must be conducted above atmospheric pressure. A temperature of 75° C and a pressure of 30 psia are considered practical. While the concentration of molybdenum and vanadium varies with different ore concentrates, a column feed composition of 0.02 wt.% molybdenum hexafluoride and 0.5 wt.% vanadium oxytrifluoride was chosen for calculation purposes.

An illustrative case for an actual column is given in Fig. 8. The stream quantities shown in the stripping section are based on:

(1) a vapor-to-product molar ratio of 3,

(2) product concentrations of vanadium and molybdenum of 1×10^{-6} mol fraction,

(3) an assumed concentration of MoF_6 of 0.03 mol fraction at the top of the column.

The calculation of theoretical plates based on MoF_6 separation indicates that 21 are required for the stripping sectionand 10 are required above the feed plate in the enriching section. Because of the limited solubility of VOF_3 in UF_6, no rectification occurs above the feed plate, since in the example chosen the vapor in equilibrium with this material has a VOF_3 concentration above the solubility limit. It is believed that very little actual solid formation would occur in an adiabatic tower under these conditions. If solids were found to be troublesome the enriching section could be eliminated entirely by moving the feed point to the top of the tower at the expense of additional plates.

The above outline of a distillation process shows that purification by this method does not appear particularly difficult.

CONCLUSIONS

Development work has demonstrated the feasibility of converting uranium concentrates to crude uranium tetrafluoride continuously in fluidized-bed equipment. Of six types of ore concentrates tested, most were highly reactive, and all were sufficiently reactive to give adequate conversion in relatively short residence times. Ore concentrates containing large percenages of sodium were satisfactorily processed to crude uranium tetrafluoride in fluidized reactors despite the sensitivity of these materials to sintering and caking.

The pilot-scale studies on crude uranium tetrafluoride production using four- and five-stage reactors indicated that simplified equipment with fewer stages would be adequate and desirable for processing these materials. With fewer stages, the presence of substantial quantities of fines in the solid feed could be tolerated, and particle size would be less important. Other work indicated that single-stage equipment could be used, especially if two reactors in series were employed for each step.

Techniques developed for size preparation of the concentrates prior to fluidization proved successful, though additional study is desirable to improve the particle strength. Only a moderate amount of particle breakup occurred during processing to uranium tetrafluoride.

Studies on the fluorination of crude uranium tetrafluoride to uranium hexafluoride showed that feed materials containing little or no sodium impurity could be processed without difficulty. Caking problems were encountered in some instances with material produced from carbonate-leached ore concentrates containing large amounts of sodium. Methods for relieving these caking troubles by the use of solid diluents and/or the use of a stirred fluid-bed reactor appeared promising. Operating variables which affect the fluorination process have been studied, and the efficiency of fluorine utilization has been determined under various conditions.

Appreciable purification of the ore concentrates occurred in each of the process steps prior to distillation, and the remaining impurities were primarily vanadium and molybdenum fluorides. Laboratory data necessary for the design of uranium hexafluoride distillation equipment was obtained. These data included vapor pressures, solubilities, and vapor-liquid equilibra for vanadium and molybdenum fluorides. Preliminary distillation experiments on both laboratory- and pilot-scale have shown that these impurities can be separated from uranium hexafluoride to produce a product of high purity. Both the molybdenum and vanadium impurities were concentrated in the upper part of the column and removed in the fore-cut. The principal vanadium species in the crude uranium hexafluoride was identified as vanadium oxytrifluoride. Though this compound has limited solubility in uranium hexafluoride, no evidence of precipitation within the distillation column itself was found.

In addition to the work reported in this paper, considerable pilot-scale development work necessary for the design of a full-scale production plant has been carried out by the Allied Chemical and Dye Corporation. This work is at an advanced stage of development and the design of most of the production equipment has been completed.

ACKNOWLEDGEMENTS

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Work on vapor-liquid equilibria, solubilities of impurities in UF_6, and some distillation experiments was carried out by W. H. Mears and co-workers at General Chemical Division, Allied Chemical and Dye Corporation.

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