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THE PREPARATION OF PURE URANIUM TETRAFLUORIDE BY A WET PROCESS

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THE PREPARATION OF PURE URANIUM TETRAFLUORIDE BY A WET PROCESS

Introduction

Uranium tetrafluoride is produced commercially by a so-called "dry process". This process consists of passing hydrogen fluoride gas over a bed of uranium dioxide in a suitable furnace at a temperature of 575°C. The following reaction takes place.

$$UO_2 + 4\ HF \rightarrow UF_4 + 2\ H_2O \qquad (1)$$

The conversion of uranium dioxide to uranium tetrafluoride is about 97 to 98% complete. Since the uranium dioxide as used contains about 98% UO_2 and 2% U_3O_8, conversion to UF_4 cannot be complete because of the presence of U_3O_8.

$$U_3O_8 + 8\ HF \rightarrow UF_4 + 2\ UO_2F_2 + 4\ H_2O \qquad (2)$$

The product obtained in equation (1) contains 98 ± 0.5% UF_4, 2 ± 0.3% UO_2F_2, and less than 0.4% UO_2 or U_3O_8.

The uranium tetrafluoride produced by equation (1) is used to obtain uranium metal by equation (3).

$$UF_4 + 2\ Mg + \text{heat} \rightarrow U + 2\ MgF_2 \qquad (3)$$

This is a thermite reaction and is subject to many variables. The attainment of a high yield of metal from this process is the result of carefully controlled conditions. Among the variables which were examined in attempting to attain the desired yield, it was thought that the presence of uranium compounds other than UF_4 would have a deleterious effect. A process was sought which would produce uranium tetrafluoride free from other compounds of uranium and incidentally free of harmful impurities.

Discussion

Two methods were investigated, both being accomplished in water phases and producing uranium tetrafluoride as a precipitate. Thus the term "wet process" was derived to describe the production of uranium tetrafluoride in a liquid medium. The methods may be represented by the following equations.

Method A. Uranium dioxide as the raw material.

Same reaction as equation (1) but in aqueous phase.

Method B. Uranium trioxide as the raw material.

$$UO_3 + 2\ HCl \rightarrow UO_2Cl_2 + H_2O \qquad (3)$$

$$UO_2Cl_2 + 2\ R + 4\ HCl \rightarrow UCl_4 + 2\ RCl + 2\ H_2O \qquad (4)$$

$$UCl_4 + 4\ HF \rightarrow UF_4 + 4\ HCl \qquad (5)$$

(R designates a reducing agent.)

A successful process for accomplishing Method A was evolved. The main difficulty encountered was the attainment of adequate agitation to insure complete reaction of materials.

In Method B, zinc was found to be the most successful reducing agent. The production technique is described in the next section.

The UF_4 produced by both methods must be dried at 700 to 800°C in an atmosphere of HF to produce an anhydrous, non-hygroscopic product. The bulk may be reduced to approach that of dry process UF_4 by treatment with HCl during low temperature drying. The drying at high temperature without HCl will also reduce the bulk, in some cases equaling that of dry process material.

The purity of the product obtained is as good or better than the dry process product except for a few elements. Even these elements will be largely removed during the thermite reaction and subsequent recasting of the uranium metal.

The yield of metal is not as high as is obtained using dry process UF_4, and the capacity of thermite equipment is reduced due to the higher bulk of the wet process product.

Experimental

The production of UF_4 was investigated using both Method A and Method B as outlined in the discussion. The product obtained in either case was a precipitate of UF_4 in a water phase together with other reaction products in solution. The UF_4 was filtered from the solution and the subsequent treatment of the UF_4 was the same in both cases. The two methods of preparation of UF_4 will be described and the subsequent treatment of the product will be considered as a unit.

Method A

Finely divided UO_2 was added to a dilute hydrofluoric acid solution while the solution was violently and completely agitated. Since the reaction involves a solid starting material and a solid product with no stable intermediate soluble stage, it is apparent that the reaction cannot proceed to completion unless the solids are kept finely dispersed in the reaction medium. If any quantity of solids is allowed to accumulate at any quiescent area in the reaction vessel, caking of the UO_2 will occur with subsequent loss of yield. One of the major difficulties in the experimental work was the attainment of the required agitation with the equipment at hand. Experiments were first conducted in a rubber-lined pot ten inches in diameter and twelve inches deep having a capacity of four gallons. Two propellor stirrers were used, each one and one half inches in diameter with three blades. One stirrer was directed toward the center of the pot and the other was directed tangentially to the periphery of the pot at right angles to the first stirrer. Thus, material which settled in the center of the pot was directed toward the outer edge where it was picked up by the second stirrer. Both stirrers were positioned near the bottom of the pot. In addition, the pot was placed on a turntable rotating at 15 rpm and in a direction opposite to the stirring action of the propellors. This arrangement effected nearly complete dispersion of the solids in the reaction medium, but some caking was unavoidable.

Seven experiments were tried using the equipment described above and the data obtained is summarized below in Table 1. In all cases the concentration of HF in the solution before adding UO_2 was 6.6% by weight. The UO_2 was added in the amount of about 1.7 pounds per gallon of solution and the excess hydrofluoric acid was 7.9% by weight. After the indicated stirring period, the reaction mixture was allowed to stand sixteen hours before filtration. The effect of particle size of the UO_2 used was found by using one material, the regular type, all of which would pass a thirty-mesh screen, and the same material, micropulverized so that eight per cent would pass a hundred-mesh screen.

TABLE 2

Expt. No.	Volume of solution gallons	UO_2 used lbs.	Source	Stirring time hours	% yield by weight of product
1	1.75	3	Micropulverized	5	93.4
2*	1.75	3	Micropulverized	2	44.5
3	1.75	3	Micropulverized	6	100.0
4	3.50	6	Regular	7	80.4
5	3.50	6	Regular	8.5	55.5
6	1.75	3	Regular	7	89.8
7	1.75	3	Regular	8	60.9

*One stirrer only; at periphery of tub.

Soon after the UO_2 was added to the acid solution, the slurry set up to a very stiff paste making stirring difficult. About one half hour later the slurry thinned out to a mixture which was easily stirred. In Experiments 1 and 2 an attempt was made to eliminate the formation of the thick slurry. The UO_2 was added in quarter portions each half hour. However, a thick slurry with subsequent thinning occurred after each addition, so this idea was abandoned.

The rate and completeness of reaction of UO_2 with hydrofluoric acid was determined in Experiments 7 and 8. All conditions were the same in each experiment except for the particle size of the brown oxide. At intervals during the reaction period, portions of the slurry were removed and the clear filtrate was titrated to determine the acid remaining in the slurry. With the logical assumption that the hydrofluoric acid is consumed only in reaction with the UO_2, the rate of reaction is shown in Table 2.

TABLE 2

Reaction Time Hrs.	Reaction Time Min.	Experiment 7 Thru 30 mesh Per cent Reaction completed	Experiment 8 80% thru 100 mesh Per cent Reaction completed
0	20	19.2	
0	40	31.6	
1	0	39.8	84.4
1	30	43.6	
2	0	51.0	88.4
3	0	58.1	
3	30		91.0
4	45		91.8
5	0	62.6	
6	30	64.4	

The advantage in the use of micropulverized UO_2 is readily apparent from the above data.

In Table 1, Experiment 7, the per cent yield of UF_4 as product obtained was 60.9%. According to Table 2, Experiment 7, the reaction was 64.4% complete after six and one half hours. Assuming about 66% conversion after eight hours, it was seen that about ten per cent of the UF_4 produced was lost in the mass of unreacted UO_2.

The UF_4 produced will remain suspended easily as a slurry because the particle size is small and the bulk is high. The UO_2 settles to the bottom rapidly under moderate stirring. Therefore, it is possible to effect a good separation of desired UF_4 and unreacted UO_2 by a process simulating decantation. The unreacted UO_2 may be dried, reground and returned to the process. This procedure is not desirable and could be made unnecessary by proper selection of raw material and reaction vessels.

After the desired reaction time in the above experiments, the precipitate was removed from the reaction mixture by use of a centrifuge. The excess hydrofluoric acid and soluble impurities were removed by washing the cake in the centrifuge. The cake is now ready for drying and further treatment. The filtrate may be fortified with concentrated hydrofluoric acid and reused in the next preparation, thus economizing in the consumption of this reagent.

Further preparations of UF_4 were made using larger equipment. A fifty-five-gallon rubber-covered barrel was placed on a larger turntable operating at twelve or twenty-four rpm. High and low speed stirrers were used. Sixty pounds UO_2, thirty gallons water and sufficient 50% hydrofluoric acid to make a ten per cent solution were used in each experiment. The agitation problem was increased due to the change in geometry of the reaction vessel. Although micropulverized UO_2 was used for all six experiments, the yields varied from forty-two to fifty-six per cent of theoretical, based upon the product obtained.

In three experiments the rate of reaction was followed in the same manner as described previously. The data is given in Table 3.

TABLE 3

Reaction Time Hours	Per Cent Reaction Completed		
	Expt. 1	Expt. 3	Expt. 5
0.5			40.2
1.0		55.7	
1.25	50.2		
1.5			78.7
2.0		62.2	
2.5			81.1
3.0		64.2	
3.25	58.6	End of stirring	
3.5			83.0
5.25	60.4		End of stirring
6.25	60.4		
	End of stirring		
Actual Yield Obtained	42.5	42.5	49.6

A similar condition prevailed in these experiments in that a large percentage of the yield was trapped in the caked, unreacted material due to inadequate agitation.

Filtration and washing were accomplished in a two-hole rubber-covered filter press. Filtration was rapid, but washing was very inefficient in this type of press. Therefore, the experiments were completed to determine the physical characteristics of the product and the chemical purity was of secondary importance.

Method B

The preparation of UF_4 by this process affords certain advantages over the physical problems of insuring complete reaction by Method A. No solid phases or precipitates were encountered until the final precipitation of UF_4. The main problem was then to remove the soluble impurities retained in the precipitate of UF_4 to secure the required purity of product.

The starting material for this process was UO_3 which was dissolved in hydrochloric acid to produce UO_2Cl_2. If a suitable reducing agent could be found to reduce the UO_2Cl_2 to UCl_4 in an acid medium, then UF_4 could be precipitated directly by adding hydrofluoric acid. Several reducing agents were investigated. Among these formaldehyde, hypophosphorous acid, hydroxyl amine hydrochloride, paraformaldehyde with and without iodine and acetone were unsatisfactory under the conditions tried. The most satisfactory reductants were stannous chloride and zinc. Zinc was selected for further development because of availability, low cost, and purity.

Experiments were conducted on a laboratory scale to investigate the most desirable method of accomplishing the steps of the reaction. Using four-mesh zinc as the reducing agent, the reaction proceeds according to the following equations:

$$UO_3 + 2\ HCl \rightarrow UO_2Cl_2 + H_2O \qquad (4)$$

$$UO_2Cl_2 + Zn + 4\ HCl \rightarrow UCl_4 + ZnCl_2 + 2\ H_2O \qquad (5)$$

$$UCl_4 + 4\ HF \rightarrow UF_4 + 4\ HCl \qquad (6)$$

In order to reduce the loss of zinc through the side reaction with hydrochloric acid in Equation (5), the hydrochloric acid was added at intervals during the reduction. Much heat was evolved during the reaction and the solution had to be cooled to prevent the loss of hydrochloric acid, the decomposition of UCl_4, and the reduction of the uranium to the tetravalent state.

The process on a larger scale may be outlined as follows. The quantities of materials are given to show the relative concentrations and excess of reagents required.

Add forty-eight pounds of 38% hydrochloric acid to fifteen gallons of distilled water in a thirty-gallon stone tub. Fifty pounds of UO_3 are added with mechanical stirring. After the UO_3 is dissolved, cool the solution to 30°C and pump over a bed of four-mesh zinc contained in a small column. The solution from the column goes through a cooler and back to the tub. The solution is continuously recycled over the zinc. The temperature is kept below 60°C by adjusting the cooling water. As reduction proceeds, six pounds of 38% hydrochloric acid are added every five minutes until fifty pounds of acid have been added. Continue recycling the solution until reduction is complete. The total time required for reduction is about seventy minutes and about thirteen pounds of zinc are consumed.

The hydrochloric acid was used in stoichiometric amount in each equation. The theoretical requirement of zinc is 11.4 pounds. The excess consumed reflects the amount of tetravalent uranium present in the solution since some over-reduction takes place. Tests show complete reduction of UO_2Cl_2. An inadvertent excess of hydrochloric acid will also cause a higher consumption of zinc. The reduction of UO_2Cl_2 is very rapid and the liberation of nascent hydrogen from the reaction of hydrochloric acid upon zinc will also aid the reduction by Equation (7).

$$UO_2Cl_2 + 2\ H + 2\ HCl \rightarrow UCl_4 + 2\ H_2O \qquad (7)$$

The solution is then filtered to remove the small amount of sludge and insoluble material which may be present. The filtrate is diluted to forty gallons in a rubber-lined barrel and heated to 40°C with a steam blow. While the solution is stirred, 15.25 pounds of anhydrous hydrofluoric acid are blown into the solution to precipitate UF_4. The theoretical requirement of hydrofluoric acid is fourteen pounds.

Since work on Method A had shown that the use of a two-hole press for filtration did not allow adequate washing and since a large amount of soluble impurities are present in the case of Method B, another scheme was used to obtain the required washing. After the UF_4 is precipitated, it is allowed to stand overnight and then the supernatant liquid is siphoned off. Forty gallons of distilled water are added and the cake reslurried. The slurry is then pumped in the press and the cake washed briefly. The cake is returned to the barrel and reslurried in forty gallons of 0.1% hydrochloric acid. The slurry is again filtered and the cake obtained is removed for further treatment.

Drying

The precipitated and washed UF_4 produced by both methods was subsequently given treatment to make it physically acceptable for the intended use of the product. The UF_4 was utilized in a thermite reaction with magnesium to produce uranium metal by Equation (8).

$$UF_4 + 2\,Mg \rightarrow U + 2\,MgF_2 \qquad (8)$$

It has been found by experience that certain physical properties of the UF_4 are essential to obtain a good yield of uranium from this reaction. The UF_4 should have low bulk, low moisture content, and should be non-hygroscopic. Uranium tetrafluoride made by the "dry process" is anhydrous, nonhygroscopic and has a bulk of 0.30 ml/gm. The UF_4 produced by the "wet process" was dried at various temperatures and by various means. The methods used and results obtained are given below. The methods used to reduce the bulk are also described. The term "bulk in ml/gm" refers to a sample of UF_4 at any stage in drying which is ground finely and placed in a graduated cylinder to determine the volume occupied by a unit weight. The cylinder is tapped on a firm surface to pack the UF_4 as much as possible without actual mechanical compression. All bulks are reported on this basis.

The moisture content of UF_4 was determined by drying at 250°C for twenty hours. It is very difficult to obtain accurate water analyses by a direct method because of the difficulty in removing the water of hydration and the danger of decomposing the UF_4 at elevated temperatures. As a result of many tests the above conditions were selected as a basis for comparison, even if the actual moisture contents were not absolute.

The moisture pickup or hygroscopicity of the UF_4 is determined by exposing a sample of UF_4 to an atmosphere of 100% humidity for twenty-four hours, then calculating the increase in weight after allowing the samples to come to equilibrium at room humidity.

It was found that the desirable properties of UF_4 enumerated above could be obtained in several ways. If UF_4 is dried at elevated temperatures in an air, CO_2 or H_2 atmosphere, decomposition of the product occurs. However, an atmosphere of HF will prevent decomposition and is necessary in high temperature drying. It was also found that treatment of the wet or dried UF_4 with hydrochloric acid and then subsequently drying will reduce the bulk of UF_4 to a value near that desired. The various experiments tried and results obtained are listed in the following tables.

TABLE 4

450 grams UF_4 from Expt. 1, Table 1,
which had been dried at 150°C for 18 hours

Expt.	ml HCl used	Bulk ml/gm	Moisture Content %	Water pickup %
1a	0	0.54	3.20	2.07
b	145	0.35	2.16	1.59
c	210	0.40	2.51	2.30

TABLE 5

UF_4 from Expt. 2, Table 1

Expt.	Weight UF_4 gm	Conc. HCl used wgt. %	HCl used ml	Drying Temp. °C	Drying Time hrs.	Bulk ml/gm	Moisture Content %	Water Pickup %
2a			0	150	16	1.08	2.56	6.85
b	120 of a	1	45	150	40	0.55	1.44	5.00
c	120 of a	3	45	150	40	0.51	1.69	3.00
d	120 of a	5	50	150	40	0.47	1.66	2.20
e	120 of a	8	45	150	40	0.45	1.68	2.50
f	120 of a	10	45	150	40	0.47	1.92	2.00
g	60 of f	5	25	150	40	0.48		
h	90 of d 90 of e		0	580 in HF	30	0.45	0.10	0.11

TABLE 6

UF_4 from Expt. 4, Table 1

Expt.	Weight UF_4 gm	Conc. HCl used wgt. %	HCl used ml	Drying Temp. °C	Drying Time hrs.	Bulk ml/gm	Moisture Content %	Water Pickup %
4a			0	200	16	0.90	0.32	6.4
b	2050	5	850	95	20	0.40	3.62	2.76
c	1550 of b		0	580 in HF	30	0.47	0.25	0.43

TABLE 7

UF_4 from Expt. 7, Table 1

Expt.	Weight UF_4 gms	Conc. HCl used wgt. %	HCl used ml	Drying Temp. °C	Drying Time hrs.	Bulk ml/gm
7a			0	95	16	0.96
b			0	140	16	0.76
e			0	235	16	0.74
d	120 of a	5	70	95	16	0.47
e	120 of b	5	70	140	16	0.45
f	120 of c	5	60	235	16	0.34

Tests of the dried product in all the above cases where HCl was used show no detectable chloride present.

Further de-bulking experiments were made on the UF_4 produced on a larger scale and referred to in Table 3. The treatment and results are shown in Table 8.

TABLE 8

Expt.	Treatment of UF_4 produced	Bulk ml/gm	Moisture Content %	Water Pickup %
1	Dried 8 hrs. at 200°C Moistened with 5% HCl Dried 4 hrs. at 200°C and 4 hrs. at 400°C in HF	0.50	0.25	0.23
2	Treated in filter press with 5% HCl. Dried 4 hrs. at 200°C and 4 hrs. at 400°C in HF	0.42	0.16	0.14
3	Same as 2	0.41	0.26	0.43
4	Treated in filter press with 5% HCl. Dried 8 hrs. at 400°C in HF	0.41	0.28	0.40
5	Treated in press with 5% HCl. Dried 16 hrs. at 95°C. Dried 8 hrs. at 500°C in HF.	0.56	0.19	0.12
6	Same as 5	0.48	0.15	0.14

Some samples of wet process UF_4 from various experiments were dried at various temperatures without treatment with hydrochloric acid. The results obtained are shown in Table 9.

TABLE 9

Sample	Drying at 150° C hours	High Temp. Drying			Bulk ml/gm	Moisture Content	Water Pick-up	Comment
		Hours	Temp.	Atmosphere				
A	20					3.52%	7.6%	
B	48					1.24		
C	22					3.04	6.78	
D-1	20				0.90	2.75	6.3	
D-2	Mill and redry D-1 at 150°C for 24 hrs.				.96	1.41		
E	23	1	600	CO_2		0.19		H_2O + HF evolved UF_4 decomposed
F	22	1	800	CO_2		0.20	0.40	Same as E
G	21	1	600	H_2	0.70	0.14	0.34	Decomposed
H	16	1	800	H_2	0.39	0.13		Decomposed and sintered
I	39	1	800	H_2	0.33			Same as H
J	20	3	800	HF	0.30			No decomposition. Sintered
K	40	3	600-700	HF	0.60			No sintering
L	18	3	800	HF	0.39			Sintered

From the data given in Tables 4 through 9 it is evident that the attainment of an anhydrous, non-hygroscopic UF_4 of low bulk by a wet process is rather difficult. However, it can be attained by drying the UF_4 in a furnace at 700° to 800°C in an atmosphere of HF for several hours. Since the equipment for the production of UF_4 by the "dry process" is identical with that used drying the "wet process" UF_4, the advantages, if any, of the "wet process" are nullified.

Use of UF_4 in Thermite Reaction

The UF_4 produced by the wet process was compared to UF_4 produced by the dry process in the thermite reaction to produce uranium metal. The results of these tests are shown in Table 10. The wet process UF_4 was dried at 500°C in HF atmosphere.

This data shows that good yields may be obtained, but that the dry process UF_4 averages about 6% better in yield. The higher bulk of the wet process UF_4 also reduces the capacity of the thermite equipment.

TABLE 10

Expt.	Type of UF_4	UF_4 Lot	Magnesium Lot	Yield of Metal %
1	Wet process	A	A	52.3
2	Wet process	A	A	83.4
3	Dry process	A	A	71.9
4	Dry process	A	B	73.6
5	Dry process	A	B	74.3
6	Dry process	A	C	61.8
7	Wet process	A	D	90.7
8	Wet process	A	D	90.7
9	Wet process	B	D	84.5
10	Wet process	B	D	84.5
11	Wet process	C	D	89.6
12	Wet process	C	D	89.6
13	Dry process	A	D	95.2
14	Dry process	A	D	88.9
15	Wet process	C	E	89.5
16	Wet process	C	E	90.3
17	Dry process	B	E	96.5
18	Dry process	B	E	96.7

Purity of UF_4 by Wet Process

Analytical results found on UF_4 produced by Methods A and B and by the dry process are given as averages in Table 11. The quantities of other impurities which are higher in wet process UF_4 than in dry process UF_4 are given in ppm.

TABLE 11

	Wet process		
	Method A	Method B	Dry Process
UF_4	98.84%	98.60%	97.53%
UO_2 or U_3O_8	0.06	0.0	0.38
UO_2F_2	1.10	1.31	2.20
Total U^{+4}	74.97	74.70	74.24
HNO_3 insol.	0.00	0.0	0.00
Fluorine	23.9	23.8	24.0
Zinc		1000 ppm	less than 2 ppm
Boron	0.5 ppm	0.15 ppm	0.1 ppm
Ca	60 ppm	15 ppm	less than 5 ppm
Na	50 ppm	5 ppm	less than 10 ppm
Fe	133 ppm	12 ppm	12 ppm

Summary

Two methods have been developed for the production of UF_4 by a wet process. However, the more involved procedure required for each method and the failure of the product to exceed the quality of that produced by the dry process eliminate these methods as competitors of the present dry process.