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**CONVERSION OF URANIUM HEXAFLUORIDE
TO URANIUM TRICHLORIDE**

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Written by: E. B. Brown

(Authorship does not imply responsibility for the ideas or experimental data reported. For the source material consult the references which appear at the end of the paper.)

INTRODUCTION

The properties of uranium hexafluoride are rather unusual. Since the triple point pressure lies above atmospheric it sublimes, attaining a vapor pressure equal to atmospheric at only 56.4 degrees centigrade. The solid may be liquified under its own vapor pressure of 1165 mm at 64.5 degrees centigrade. Chemically the compound is extremely reactive as a fluorinating agent; when it acts in this capacity it is reduced to the highly stable tetrafluoride. The hexafluoride reacts with almost all metals, at least at elevated temperatures. Any resistance that a metal possesses toward the vaporous compound is due to the formation of a protective coating of fluoride on the surface of the metal. In this respect nickel, copper, and aluminum seem most resistant to corrosion.

For conversion of the uranium hexafluoride to other compounds such as the oxides or chlorides, a direct, one-step process was obviously desirable. However, the tendency of the hexafluoride to lose two of its fluorine atoms upon the slightest provocation caused such attempts to result in conversion to the unreactive tetrafluoride⁽¹⁾. The quantitative transformation of this substance into uranium tetrachloride is exceedingly difficult. Small amounts of uranium tetrafluoride may be converted to uranosic oxide by lengthy ignition in oxygen or air, but this is not practical for quantities larger than a few grams. The necessity for utilizing less direct methods for the uranium hexafluoride conversion was apparent.

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INTRODUCTION

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An entirely satisfactory method was worked out by taking advantage of the the dissolution and hydrolysis of the hexafluoride by water to form ionic uranyl fluoride and hydrofluoric acid.

It is then possible by one or more precipitations, to quantitatively obtain the uranium as a fluoride free compound which may be simply ignited to the trioxide. Other substances such as the chlorides may be easily derived from the trioxide by well-known procedures.

The dissolution-hydrolysis step was accomplished in two ways. In one case the uranium hexafluoride was liquified by heating in a sealed container and ejected quickly by its own vapor pressure into water. Such a system is especially desirable when large quantities of material are handled. A second method, designed for smaller unit operations, consists of cooling the volatile compound to reduce its vapor pressure followed by dissolution of the solid material. ⁽²⁾
⁽³⁾

Precipitation of uranium from the resulting solution has also been carried out by two separate procedures. The precipitations in each case are inhibited by the presence of fluoride ion, causing the formation of a complex ion species with uranyl ions. This disadvantage has been overcome by imposing carefully controlled reaction conditions. In one case a peroxide precipitation is made after the fluoride concentration has been reduced by initial formation of the extremely insoluble ammonium diuranate. ^(4,5)

*The precipitate obtained with ammonium hydroxide actually exists as ammonium diuranate for only a short period--gradually forming monouranate or uranate mixtures. For simplicity the precipitate is commonly referred to as ammonium diuranate.

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The ammonium diuranate is then dissolved in nitric acid, and the uranium peroxide precipitated in the presence of a small amount of residual fluoride ion under carefully controlled conditions.

A second method utilizes a single, direct peroxide precipitation again made according to a specially designed procedure.

DISCUSSION

Dissolution of Uranium Hexafluoride

Several methods were investigated for removing and dissolving uranium hexafluoride from shipping cylinders. When sublimed through liquids it was absorbed very slowly. A spray caused by vigorous stirring of water absorbed the hexafluoride vapors at only a fair rate. The vapors were found to condense readily on cold solid surfaces, and could then be dissolved easily in water if the surfaces were large and flat. In narrow areas, such as pipes or between beads, there was considerable clogging, and solution of the condensed solid was difficult.

The first method finally adopted was designed for removal of the uranium hexafluoride from iron shipping cylinders containing approximately fifty pounds of material. This process was based on liquification of the hexafluoride in the cylinder and running it under the surface of water. Later, a procedure for dissolution of solid hexafluoride was designed to handle material received in approximately 1500 gram lots.

(2)

Liquid Dissolving Process.--A laboratory model of the cylinder and dissolver for uranium hexafluoride is shown in Figure 1. It is capable of dissolving 250 grams of liquified charge in 5-60 seconds, depending on the valve adjustment. In this model two liters of water are placed in the

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dissolver and undergo a temperature rise of about 15 degrees centigrade due to heat of solution of the hexafluoride. It works equally well with water initially at temperatures from 0-85 degrees centigrade. In full scale operations (8,9) 50 pounds of liquified hexafluoride were released from the iron shipping cylinders through a monel pipe to a 20 gallon dissolver.

For ease of construction, the laboratory apparatus was made mainly of monel, and a considerable amount of this metal was dissolved by the hydrofluoric acid formed in the dissolver. Corrosion tests were then made to find material most resistant to attack by the dissolver solution. (9,10,11,12) (10) Lead and later silver were found to be satisfactory and were used in constructing the larger units.

(3)
Solid Dissolving Process.--The flowsheet for this process is diagrammed in Figure 3. The shipping container is made entirely of silver and the dissolver is made of stainless steel with the entire inside lined with 1/8 inch silver sheet. The silver shipping bottle contains 1500 grams of hexafluoride. This is cooled in dry ice reducing its vapor pressure to approximately one micron. The bottle is then unsealed and suspended by means of silver lugs in the upper part of the dissolver which is designed to hold 3750 ml of water out of contact with the suspended bottle. Dissolution of the 1500 grams charge is accomplished by tipping and rocking the dissolver for one hour in a water bath held at 75 degrees centigrade; at somewhat lower temperatures the material dissolves very slowly.

Precipitation as the Ammonium Diuranate

Concentrations of the resulting solutions from either dissolving process may be adjusted, if necessary, to any value most ideal for precipitation by

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simply diluting with distilled water. With the solution from the large containers the two-step purification was utilized. Precipitation of the basic uranate and uranium peroxide from these solutions encounters only one major difficulty. Fluoride ions form associated molecules with the uranyl ions which are stable enough to substantially interfere with the peroxide precipitation and to a lesser extent with the ammonia precipitation. The fluoride interference is reduced in the ammonia step by using exceedingly high concentrations of ammonia and in the peroxide precipitation by complexing the small amount of residual fluoride ion with aluminum ions.

(4)

Ammonia Precipitation Process.--In this precipitation the uranium hexafluoride solution, containing 203 grams of uranium per liter, is poured quickly and with gentle stirring into 2.4 times the equivalent amount of concentrated ammonia necessary to form $(\text{NH}_4)_2\text{T}_2\text{O}_7$ and neutralize the HF. The reaction raises the temperature of the mixture to about 65 degrees centigrade. After coagulation for ten minutes at this temperature an additional 5.4 equivalents of concentrated ammonia are added, and the mixture cooled to room temperature. Coagulation with a small amount of somewhat diluted ammonia gives a precipitate which is easily settled, washed and filtered. The large excess of ammonia added later is necessary to make the precipitation complete in the presence of fluoride ion.

(4)

Completeness of Precipitation.--Under the conditions described above the precipitation of ammonium diuranate in the presence of fluoride is as complete as the standard quantitative method in the presence of nitrate. The necessary factors for a high yield in a solution containing fluoride were found to be 1. large excess of ammonia, 2. low concentration of water, 3. low concentration of nitrate ion--if any. Experimental confirmation for these

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conclusions may be found in Table 1. The percentage uranium recovered in all these experiments are calculated by comparing with standard gravimetric determinations of uranyl nitrate solutions.

(4)
Fluoride Content of the Precipitate.--The fluoride content of the uranate precipitate, formed in the manner described above, is about 1.5% after moderate washing by decantation or on a filter. This means that the fluoride percentage based on uranium has been reduced from almost 50% to 2%. The wash used was a water solution containing 2% ammonium nitrate and 2.5% ammonium hydroxide. Prolonged washing treatment removes but little more of the residual fluoride. The value of 1.5% is low enough, however, to insure a proper precipitation when the cake is dissolved and the uranium precipitated with hydrogen peroxide, using aluminum to complex the fluoride ion.

If necessary, further reduction of the fluoride content may be accomplished in two ways; first by dissolving in nitric acid and reprecipitating as the basic uranate or second by forming U_3O_8 above 900 degrees centigrade.

(4)
Settling and Filter Rates.--The best method found for obtaining a precipitate which settled and filtered quickly was to precipitate and coagulate it in the presence of a low concentration of excess ammonia. This method is used in the last experiments in Table 2. The remainder of the ammonia necessary to completely precipitate the uranium may be added later. Several wetting agents, coprecipitation with aluminum and addition of sulfates were found ineffective in speeding the handling of the precipitate formed in this manner.

(4)
Corrosion Tests.--Pfaudler glass was tested for corrosion by placing strips in platinum dishes containing precipitates made with 80% of the UF_6 concentration recommended above and five times theoretical ammonia. The

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portion of the glass in the solid which had settled was visibly etched while that in the supernatant liquid remained smooth. Test samples running for twelve hours at 70 degrees centigrade were corroded at a rate of 0.033 inches per year. Twenty-four hour tests at room temperature indicated a loss of only 0.002 inches per year. Pfaudler glass was used later in pilot plant precipitations and was found suitable for continuous production operations.

(5)

Peroxide Precipitation of Redissolved Ammonium Diuranate

The ammonia precipitate derived from the previously described process is dissolved in nitric acid and converted to uranium peroxide at a pH of 3 in the presence of aluminum ions, sulfate ions and aerosol OT. An easily settled and filtered precipitate is formed with the hydrogen peroxide which leaves less than 5 mg of uranium per liter in solution. Less than 0.08% fluoride ion and less than 0.5% sulfate ion are absorbed on the precipitate. The aluminum content varies between 0.3 and 0.03%. Pfaudler glass lining is successful for the peroxide precipitation as well as the ammonia process.

Process

1. Ammonium diuranate is dissolved in concentrated nitric acid in the proportions of 2 grams of precipitate per ml of acid.
2. Eight ml of water are added for each gram of precipitate.
3. Six times the $\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ needed to form AlF_6^{3-} is added and the solution then made 0.02% in aerosol OT.
4. The pH is adjusted to 3 with concentrated ammonium hydroxide.
5. With considerable stirring 30% hydrogen peroxide and concentrated ammonium hydroxide are added simultaneously over a period of one-half hour holding the solution below 35 degrees centigrade and the pH as nearly as

possible at 3 until the theoretical hydrogen peroxide has been added. Just before this point is reached the pH decreases rapidly and the ratio of ammonia to hydrogen peroxide must be increased. Then the pH rises rapidly and the addition of ammonia is discontinued. Thirty ml of excess hydrogen peroxide are then added for each liter of solution.

6. The supernatant is decanted and the precipitate washed twice by decantation with volumes of 1% hydrogen peroxide solution equal to the original volume of solution.

7. The precipitate is filtered on sharkskin paper with 10 inch reduction in pressure, and washed with 1% hydrogen peroxide solution.

The concentrations of pertinent ions in the system to be precipitated computed on the final volume are as follows: 0.34M uranium, 0.84M nitrate, 0.05-0.10M fluoride, 0.05-0.10M aluminum ion and 0.075-0.15M sulfate.

(5)

Quantitativeness.--The amount of hydrogen peroxide employed insures a quantitative precipitation if the pH of the system is maintained at 3 and proper amounts of aluminum ion are employed. The importance of accurate pH adjustment is shown by the results in Figure 3. At pH values below 3 the precipitation becomes rapidly non-quantitative. Whereas at values above this, filtration rather than quantitativeness is impaired, probably due to the formation of small amounts of aluminum hydroxide or ammonium diuranate. In these experiments all factors outlined under "process" were held constant except the hydrogen ion concentration.

Similar runs were made varying the fluoride ion concentration and the aluminum ion-fluoride ion ratio. From the results as listed in Table 5, a 1:1 molar ratio of aluminum to fluorine was selected as the most satisfactory proportion.

Under the specified conditions the amount of uranium left in the effluent

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is less than 5 mg/l and that in the washings negligible, providing a total recovery of better than 99.99%.

Sedimentation and Filtration.--It was found that the sedimentation and filtering properties of the uranium peroxide as derived from the dissolved basic uranate precipitation is affected by the rate of hydrogen peroxide addition, pH during the reaction, presence of sulfate ions and the presence of aerosol OT. The temperature at which the precipitation is carried out seems to have no influence upon these properties. A hydrogen peroxide addition time of 30 minutes seemed optimum from the experiments listed in Table 4, and a pH value of 3 appeared most suitable from the graphical results shown in Figure 4 and also those in the previous Figure 3. The effects of sulfate ions and aerosol OT are given in Table 5. From these results an aerosol concentration of 0.02% and a sulfate concentration between 0.075 and 0.15M were chosen as optimum operating quantities.

(6,7)

Single-Step Direct Precipitation as Uranium Peroxide

This process consists of diluting the water solution of uranium hexafluoride from the solid dissolving process with a prepared solution of aluminum nitrate such that the final solution is about 5% with respect to uranium and the F/Al ratio is exactly the desired value. The solution is then treated with hydrogen peroxide in a manner which produces a minimum amount of aluminum and fluoride on the precipitate, a minimum amount of uranium in the effluent, and minimum settling and filtering time for the slurry.

The concentrations of ions in the system for this peroxide precipitation differ from those of the previously described process in that the uranium

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is more dilute and the fluoride much more concentrated, i.e. 0.21M U as compared to 0.34M U and 1.26M F as compared to 0.05-0.10M F.

Process

1. To a 5% solution of uranium as uranium hexafluoride in water add enough aluminum nitrate to make the mole ratio F/Al equal to 1.
2. Adjust the pH of the solution to 1.5.
3. Add hydrogen peroxide theoretically required for reaction at a slow enough rate so that the pH can be held constant at 1.5 by simultaneous addition of ammonium hydroxide. Reaction time of approximately 10-15 minutes is reasonable.

Then add excess hydrogen peroxide corresponding to 0.5M. This equals 50 cc 30% hydrogen peroxide per liter of solution.

4. From a 10% solution add 1 gram aerosol OT per liter of solution.
5. Filter slurry and wash with approximately equal volume of 2% ammonium nitrate, 2% hydrogen peroxide solution.

Quantitativeness.--In Table 6 experiments are presented which show the effects that variation of pH and F/Al ratio have on the precipitation. The precipitation is successful at remarkably high F/Al ratios with the concentration of uranium in the effluent not being greatly affected by variation of pH over the range 1.5 to 3.5. For optimum performance a F/Al ratio of 1 was chosen to give the least amount of fluoride on the precipitate (see Table 7). A precipitation pH of 1.5 must then be used in the presence of this aluminum concentration since at higher pH values a gel like precipitate containing aluminum hydroxide is obtained. The data in Table 6 indicate that under these conditions less than 5 mg/l of uranium are left in the filtrate providing a total uranium recovery of about 99.99%.

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Filtration and Sedimentation.--Chloride and sulfate ions had previously been shown to have a desirable effect on the nature of the precipitate. The addition of chloride or sulfate was not used in this particular process because recovery of uranium from the effluents by ether extractions was planned. In such case the presence of these ions would be very troublesome.

Wetting agents alone, however, proved to give satisfactory precipitates. Some experiments in which the sedimentation curves were determined for various wetting agents are presented in Figure 5. In general there is a correspondence between the rates of sedimentation and filtration. However, high aerosol, 0.5% for example, gives a precipitate which settles very much like the 0.05 and 0.1% systems but filters poorly. The optimum concentration appears to be 0.1% aerosol for 5% uranium hexafluoride solutions containing aluminum nitrate. Most advantageous and consistent results are derived by adding the aerosol after precipitation with hydrogen peroxide rather than prior to it.

(6,7)

Precipitate Purity.--In order to determine how effectively fluoride and aluminum are removed from the uranium by precipitation and washing procedures similar to those discussed under "process", the experiments outlined in Table 7 were performed. As would be expected the percent Al on the uranium peroxide cake decreases with decrease in pH. The fluoride content of the precipitate in general increases with increase in F/Al ratio. Using a pH of 1.5, F/Al ratio of 1 and a washing procedure similar to the one recommended under "process" the fluoride content of the cake is normally less than 0.3% and the aluminum less than 0.1%.

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EXPERIMENTAL

Almost all of the experimental results have been determined on small laboratory scale batches. Later trials in pilot plants or production units have however, served to confirm the laboratory results. Small changes in either design or method between laboratory and pilot plant will be noted in the experimental section.

Dissolution of Uranium Hexafluoride

(2)

Liquid Dissolving Process.--A laboratory model of the cylinder and dissolver is shown in Figure 1. With all valves closed except 2, the hexafluoride container is held at 75°C until the uranium hexafluoride is liquified under its vapor pressure of 2.1 atmospheres. With the stirrer in operation valve 1 is opened and the hexafluoride is forced into the dissolver. When the cylinder is emptied, 1 is closed and the line flushed with nitrogen admitted through 5. Valve 5 is then closed, excess pressure released through 4, and the solution of uranyl fluoride and HF drained through 3 into a precipitator.

The pilot plant apparatus, aside from being built for larger capacity, had a somewhat different design. In this model the hexafluoride drain line entered the top of the dissolver into a silver funnel arrangement just above the surface of the water.

(3)

Solid Dissolving Process.--The flowsheet for this process is diagrammed in Figure 2. All of the experimental work was performed on a full production basis. Figure 2 represents a break-down of the typical production operations including the sampling and weighing steps for plant material balance. The entire procedure consists of the following steps:

A. Arrival of the silver shipping bottle in cadmium sheath packed in dry ice.

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- B. Removal from dry ice and sheath.
- C. Defrosting of bottle in alcohol.
- D. Weighing of bottle under bell jar in nitrogen atmosphere.
- E. Repacking in dry ice until ready for use.
- F. Opening of silver bottle.
- G. Placing of silver bottle in dissolver after charging dissolver with water.
- H. Closing and sealing dissolver.
- I. Rocking agitator to effect solution of the hexafluoride.
- J. Opening dissolver, removing, sampling, weighing, and transferring to a precipitating tank.

(4)

Precipitation of the Ammonium Diuranate

Completeness of Precipitation.---In Table 1 uranium yields are compared with those obtained by the standard gravimetric method. To simulate solutions of uranium hexafluoride, samples of uranium trioxide of various sizes were carefully weighed and dissolved in their equivalent weights of HF in platinum dishes. Water was added to each to give concentrations of 203 g uranium per liter. The solutions were then poured into beakers containing 2.4 times the theoretical amount of ammonium hydroxide and further additions, to give the tabulated concentrations, were made after heating and coagulation. In all experiments the same final total volume of liquid was attained, by proper adjustment of reagent volumes. The uranium recovery in each case is computed on the yield obtained from a gravimetric determination on another sample of the same uranium trioxide dissolved in nitric acid. Analyses were performed by the alpha count method on the effluents from experiments 4 and 5. Less than 0.6 mg uranium per liter was found in both cases.

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FIGURE 1

DISSOLVER FOR LIQUID URANIUM HEXAFLUORIDE

A. TANK CONTAINING UF_6
 B. RES. WIRE HEATING SYSTEM
 C. LIGHTNING MIXER

D. D2O GASKET
 E. MONEL REACTOR TANK
 1-5. VALVES

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FIGURE 2 DISSOLVING OF SOLID URANIUM HEXAFLUORIDE

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Table 1

Effect of Various Factors on Quantitative Ammonia Precipitation

<u>Experiment</u>	<u>(NH₄)₂U₂O₇ per Liter Final Solution gms</u>	<u>NH₄OH x Theoretical</u>	<u>Addition Agent</u>	<u>Uranium Precipitated %</u>
1	38.6	13	none	100.02
2	38.6	13	none	100.1
3	38.6	10	none	100.03
4	62.0	7.8	none	100.01
5	62.0	7.8	none	100.02
6	5.05	5	none	99.91
7	25.7	5	none	99.92
8	38.6	5	none	99.91
9	38.6	3	none	99.72
10	38.6	1.5	none	99.50
11	5.05	5	48cc HNO ₃ /L	99.82
12	25.7	5	48cc HNO ₃ /L	99.88
13	38.6	5	48cc HNO ₃ /L	99.80
14	62.0	6	none	99.95

Settling and Filter Rates.--In making the precipitations described in Table 2 the concentrated water solution of uranium hexafluoride at room temperature was poured over a period of two to three minutes with slow stirring from a platinum dish into a beaker containing the water, ammonia, wetting agents, etc, at various temperatures. The sedimentation was measured on 75 cc of well stirred slurry in a 100 cc graduate at room temperature. The filter rate was estimated by filtering 50 cc of slurry through paper on a 50 mm funnel with a 10 inch reduction in pressure. Lowering the pressure an

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Table 2

Sedimentation and Filter Rates of Ammonium Diuranate Precipitates

Exp.	Conc. Orig. UP ₆ gm U/liter	(NH ₄) ₂ U ₂ O ₇ per liter final solution gm	NH ₄ OH		Initial Temp. NH ₄ OH °C	Coag. Temp. °C	Coag. Time min.	Additions etc.	Settling Time to 1/2 vol. min.	Filter Time for 50 ml min.
			x Theor. During Coag.	x Theor. final						
1	203	62	7.8	7.8	25	60	20	Settle & Filter hot	45	7.2
2	203	62	7.8	7.8	30	60	20	Settle & filter hot	115	4.0
3	203	62	7.4	7.4	45	60	5	0.02% Aerosol OT	33	0.75
4	203	62	7.4	7.4	25	65	25	0.05% Naccanol	immens. slow	2
5	203	62	7.4	7.4	25	45	5	0.02% Aerosol OT	70	1.9
6	203	62	7.4	7.4	38	59	5	0.02% Santomeres	51	1.7
7	203	62	7.8	7.8	45	60	5	0.02% Gelatin	--	1.5
8	203	38.6	13	13	40	60	5	0.02% Aerosol OT	--	2.8
9	203	62	2.4	7.8	40	58	5	none	3.5	--
10	203	62	2.4	7.8	45	68	5	none	3.1	1.0
11	203	63	2.8	7.8	25	70	10	none	2.1	0.63
12	203	38.6	2.4	13	20	65	10	none	4.0	1.0
13	203	38.6	2.4	13	30	65	10	none	3.3	0.61
14	203	38.6	2.5	13	30	65	10	none	1.5	0.39

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additional 10 inches had little effect. The paper used up to run 9 was ~~sharkskin~~. This generally gave cloudy effluents so No. 40 Whatman was used thereafter. A canvas cloth on an Oliver type filter was successful in ~~plant work~~.

(5)

Precipitation of Redissolved Ammonium Diuranate

For all the precipitations solutions of ammonium diuranate were prepared by dissolving UO_3 in HNO_3 and adjusting to the desired pH with NH_4OH . The exact quantity of ammonium ion present is not the same in all experiments but its effect is negligible.

quantitativeness.--Except for pH variation the experiments in Figure 3 were carried out according to the method described under "process" upon solutions 0.34M in uranium, 0.84M in nitrate, 0.07M sulfate and 0.05M in fluoride and aluminum.

Precipitations in Table 3 were made according to the "process" method on systems containing the various constituents given in the table. These results show the effect of different fluoride ion and aluminum ion concentrations on the quantitativeness of the uranium peroxide precipitation.

The analyses for uranium in the effluents were obtained by removal of reducible metals in a mercury cathode cell and titration after reduction of the uranium to a tetravalent state by a Jones reductor.

FIGURE 3 EFFECT OF pH ON CONCENTRATION OF U IN FILTRATES AT 25° FOR SYSTEM
 $U=34M$, $NO_3=34M$, $SO_4=075M$, $F=AL^{+0.05M}$

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Table 5

Effect of Fluoride and Aluminum Ions on Peroxide
Precipitation of Redissolved Ammonium Diuranate

Conc. U M	Conc. of Added Ions in Moles per liter					U in Filtrate mg/l
	H_2O_2	F^-	Al^{+3}	NO_3^-	NH_4^+	
0.34	0	0	0	1.1	1.2	5.7
0.34	0.03	0	0	1.1	1.3	3
0.34	0.06	0	0	1.1	1.2	3
0.34	0.09	0	0	1.1	1.4	4
0.34	0.18	0	0	1.1	1.6	3
0.34	0	0.05	0	1.1	1.2	4
0.34	0	0.10	0	1.1	1.2	24
0.34	0	0.20	0	1.1	1.3	108
0.34	0	0	0.03	1.1	1.1	4
0.34	0	0	0.10	1.1	1.0	6
0.34	0	0.05	0.05	1.1	1.1	3
0.34	0	0.05	0.10	1.1	1.0	5
0.34	0	0.20	0.05	1.1	1.2	10
0.34	0	0.20	0.20	1.4	1.1	7

Sedimentation and Filtration.--In the experiments of Table 4, Figure 4, and Table 5, methods were used for precipitating the simulated diuranate solutions, 0.34M in uranium, as previously described under "process", varying certain ionic concentrations according to the values listed in the tables or figures themselves.

The filtration properties were determined by filtering 200 cc of slurry through a cylindrical glass tube 1-1/4 inch in diameter provided with a fine

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fibre glass cloth at 10 inches of mercury below atmospheric pressure. The quantity called filter time is defined as the time required for the surface of the slurry to pass a fixed mark near the bottom of the filter tube.

The sedimentation properties were determined by filling a 100 ml graduate with slurry and recording the volume of precipitate as a function of time. The sedimentation volume, V_s , is the volume of the precipitate on long standing. If one calls the initial volume of slurry V_0 , then the sedimentation half time is defined as the time required for the precipitate to settle to $(V_0 - V_s)/2$.

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FIGURE 4 EFFECT OF pH ON FILTER RATE AT 25°C
FOR SYSTEM

$U=3.4M, NO_3^-=84M, SO_4^{2-}=075M, F^-=AL^3=05M$

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Table 4

Effect of Hydrogen Peroxide Addition Time
on Settling and Filtering Rate

<u>Exp.</u>	<u>H₂O₂ Addition min.</u>	<u>Filter Time min.</u>	<u>Sed. Vol. ml</u>
30	4	1.25	28
29	8	0.45	17
32	16	0.40	15
33	32	0.35	11

Table 5

Effect of Sulfate and Aerosol
on Settling and Filtering Rate

<u>Exp.</u>	<u>SO₄²⁻ Conc. M</u>	<u>Aerosol %</u>	<u>Filter Time min.</u>	<u>Sed. Half Time min.</u>
200	0	0	9.2	21
205	0	0	4.9	20
208	0.03	0	5.3	13
209	0.06	0	3.2	9
210	0.18	0	1.1	6
211	0.06	0.02	2.9	0.4
116*	0.10	0.02	0.50	---
117*	0.10	0.02	0.45	---
118*	0.10	0.02	0.17	---
119*	0.10	0.02	0.25	---

*In these experiments sedimentations were so rapid half time was not measured.

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(6,7)

Single-Step Precipitation as Uranium Peroxide

To simulate solutions of uranium hexafluoride uranium trioxide was dissolved in the proper amount of hydrofluoric acid.

Sedimentation and Filtration.--Except for changes in kind and amounts of wetting agents the solutions and method used for the experiments in Figure 5 are exactly similar to those outlined under "process" for the one step precipitation method. In general there is a correspondence between the rates of sedimentation and filtration.

Quantitativeness.--The experiments in Table 6 were also made according to the general procedure outlined under "process" except for changes listed therein. The table demonstrates the effects of pH and F/Al ratios upon the quantitativeness of the precipitation. Uranium in the effluent was determined by colorimetric analysis.

Table 6

Effect of pH and F/Al Ratios on
the Single-Step Peroxide Precipitations

<u>pH</u>	<u>F/Al mole ratio</u>	<u>Aerosol %</u>	<u>U in Filtrate mg/l</u>
3.5	3	0.1	1150
3.5	2.5	0.1	82
3.5	2	0.1	28
3.5	1	0.1	21
3	2	0.1	28
2.5	2	0.05	21
2	3	0.1	41
2	2.5	0.1	33
2	2	0.1	19
1.5	3	0.1	22
1.5	1	0.1	< 4
1.5	1	0.1	< 4

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FIG. 5 SEDIMENTATION CURVES FOR SYSTEM
 U=5% F=1.3M AC=0.65M

262 f 4

(6,7)

Precipitate Purity.--In Table 7 the solutions, precipitation method, and washing method were similar to those described under "process" for this system. Aluminum on the precipitate was determined gravimetrically by dissolving the peroxide sample in nitric acid and precipitating the aluminum hydroxide with excess ammonium carbonate. Fluoride analysis were made according to the Willard distillation method using thorium nitrate titration with sodium alizarin sulfonate as the indicator.

Table 7

Contamination of the Uranium Peroxide by Fluoride and Aluminum

<u>pH</u>	<u>F⁻ M</u>	<u>F/Al mole ratio</u>	<u>F on Ppt. %</u>	<u>Al on Ppt. %</u>
2.5	1.26	1.5	.57	0.27
2.5	1.26	1	.24	0.67
2	1.26	1.5	.37	0.44
2	1.26	1.0	.50	0.23
2	1.26	1.0	.21	---
1.5	1.26	2.5	1.60	0.05
1.5	1.26	2.0	1.08	0.10
1.5	1.26	1.5	0.68	0.18
1.5	1.26	1.0	0.28	0.08
1.5	1.26	1.0	0.11	---

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SUMMARY

Methods for almost quantitative conversion of uranium hexafluoride into uranium trioxide have been described whereby the hexafluoride is first dissolved in water and the uranium subsequently precipitated from the solution as a nearly fluoride free compound. Uranium trioxide is then formed by a simple ignition process.

Dissolution of uranium hexafluoride has been accomplished in two ways; either by dissolving the compound in water from its liquid state or from its solid state.

Precipitation from the resulting uranyl fluoride has also been performed according to two procedures. In one case the uranium is separated from most of the fluoride ion by initially precipitating as ammonium diuranate and precipitation of uranium peroxide is carried out on the redissolved cake. In the other method the separation is carried out by a one-step uranium peroxide precipitation, using a low pH and sufficient amounts of aluminum ions to overcome the disadvantageous fluoride effect. In both cases greater than 99.9% recovery of uranium is attained.

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