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STUDIES ON THE PREPARATION OF PURE URANIUM TETRAFLUORIDE FROM CRUDE SODIUM DIURANATE

by

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INTRODUCTION

1.1. Among the uranium halides, uranium tetrafluoride is the most important material for the production of uranium because it is the easiest to prepare and handle, is the most stable, and undergoes autothermic reduction with calcium or magnesium[1]. It can be prepared from UO_2 and and other compounds of uranium by a number of processes. Aqueous solutions of uranyl salts can be reduced photochemically[2], electrolytically[3] or by stannous chloride[4] in presence of hydrofluoric acid to give UF_4. Generally it is prepared by the treatment of uranium dioxide with hydrofluoric acid or anhydrous hydrogen fluoride[5]. Ammonium fluoride and ammonium bifluoride[6] have also been used for this purpose. It is reported that the nature and yield of UF_4 prepared from UO_2 is greatly influenced by the method of preparation and the physical characteristics such as surface area, surface sintering and lattice dimensions[7] of the latter.

1.2. Ruff and Keim[8] and Henne[9] observed that fluorinated hydrocarbons could be used to convert many metal oxides into their fluorides. The reaction of various uranium oxides with different freons has been investigated by the Brown University group[10] who noticed that the physical characteristics of the UF_4 obtained by the freon reaction were different from those of the UF_4 got by hydrofluorination. Booth and co-workers[11] and Cacciari et al[12] have studied the reaction of UO_3 with freon-12 and found it technologically and economically advantageous.

DISCLAIMER

1.3. Uranium tetrafluoride used to prepare the uranium metal required in nuclear reactors should be free from various impurities, chiefly the rare earths, cadmium and boron. Crude sodium diuranate is one of the major starting materials for the preparation of pure uranium salts. It is obtained in India, at present, from the crude UF_4 which is a by-product of the thorium industry[13]. In general, crude sodium diuranate is converted to crude uranyl nitrate which is purified by solvent extraction with ether, hexone or TBP. The uranyl nitrate is converted to UO_3 which is reduced at 650-700°C by hydrogen to UO_2. The dioxide is ultimately converted to UF_4 by hydrofluorination. The present work deals with the studies and observations made in this laboratory to prepare pure UF_4 from crude sodium diuranate by two different methods. Part I describes the method based on the formation of a soluble complex of the type $M_3UO_2F_5$ which is converted by hydrogen peroxide to an insoluble peroxy complex of the type $M_4U_4O_{15}F_6 \cdot XH_2O$ where $M = K, NH_4$ or 1/2 Ba as reported by Bolton[14] (1866), Baker[15] (1879) and Lordkipanidze[16] (1900) and the subsequent reaction of the ammonium form of the peroxy complex of uranium with freon-12. Crude sodium diuranate was dissolved in nitric acid and the resulting crude uranyl nitrate solution was treated with ammonium fluoride. The precipitated fluorides of thorium, rare earths etc., were filtered off and the filtrate containing uranium and iron as complex fluorides was treated with hydrogen peroxide and ammonia. The uranium precipitated as ammonium uranium peroxy fluoride while iron remained behind in solution. The peroxy complex of uranium was filtered, washed, dried and heated in a current of freon-12 to get uranium tetrafluoride, Fig.1(a).

1.4 Part II describes the method in which crude sodium diuranate was treated as described above to get ammonium uranyl fluoride and the resulting solution was reduced photochemically (by sunlight) in presence of a suitable reducing agent like alcohol. The precipitated ammonium uranium fluoride (NH_4UF_5) was filtered, washed, dried and then decomposed in vacuum at 350°-400°C to get uranium tetrafluoride, Fig.1(b). In this paper the first method is described in detail and the observations of the second method are given in brief.

PART I

Preparation of UF_4 by the reaction of ammonium uranium peroxy fluoride with freon-12

2. Preparation of ammonium uranium peroxy fluoride:

2.1. The conditions for the separation of uranium from rare earths, thorium and iron have been reported earlier by the authors[17]. It was found that uranium could be separated from thorium and rare earths at $pH \leqslant 3.0$ and from iron at pH 6-6.5 from solutions having U_3O_8: ThO_2 + rare earths oxides $\geqslant$ 0.1 and U_3O_8: $Fe_2O_3 \geqslant$ 1.0 and $U_3O_8 \geqslant$ 0.45 g/L. Based on this data, the preparation of ammonium uranium peroxy fluoride was carried out using 5 lbs. batches of sodium diuranate.

2.2. 5 lbs. of sodium diuranate were treated with 1350 c.c. of nitric acid (ρ = 1.42) and the insoluble matter was filtered off. The filtrate was diluted to 35 litres and 1250 gms of ammonium fluoride were added to complex U, Th, rare earths and iron according to the equations 1 to 4.

$$UO_2(NO_3)_2 + 5\,NH_4F \longrightarrow (NH_4)_3\,UO_2F_5 + 2\,NH_4NO_3 \quad \text{-- (1)}$$

$$Th(NO_3)_4 + 4\,NH_4F \longrightarrow ThF_4 + 4\,NH_4NO_3 \quad \text{-- (2a)}$$

$$Th(NO_3)_4 + 5\,NH_4F \longrightarrow NH_4\,ThF_5 + 4\,NH_4NO_3 \quad \text{-- (2b)}$$

$$R(NO_3)_3 + 3\,NH_4F \longrightarrow RF_3 + 3\,NH_4NO_3 \quad \text{-- (3)}$$

(R = Rare earths)

$$Fe(NO_3)_3 + 6\,NH_4F \longrightarrow (NH_4)_3\,FeF_6 + 3\,NH_4NO_3 \quad \text{-- (4)}$$

The dilution before the addition of ammonium fluoride was necessary to prevent the precipitation of the ammonium uranyl fluoride as its solubility in water at room temperature is only about 100 gms/L. The precipitated rare earth and thorium fluorides were allowed to settle down, the supernatant solution was decanted and the rest of the slurry was filtered and washed with water till the fluoride precipitates were completely free from uranium. The filtrate was then treated with 144 c.c. of 30% hydrogen peroxide to precipitate the peroxy complex of uranium according to the equation

$$4\,M_3UO_2F_5 + 4\,H_2O_2 + 6\,MOH \longrightarrow M_4U_4O_{15}F_6 + 14\,MF + 7\,H_2O \quad \text{-- (5)}$$

on the assumption that the peroxy complex conforms to the general formula $M_4U_4O_{15}F_6.XH_2O$. The pH of the solution was adjusted to 6-6.5 by the addition of ammonia. The precipitate was filtered in a pressure filter at 40 p.s.i. and the cake was dried at 80°C in a tray drier. The yield of the peroxy complex from a few experiments are given in table I and the settling and filtration characteristics of the fluoride slurries are given in Fig.2 and Fig.3.

Table I

Yield of ammonium uranium peroxy fluoride

Sodium diuranate taken	Yield of ammonium uranium peroxy fluoride	U_3O_8 in Sodium diuranate	U_3O_8 in Peroxy complex	Uranium recovery
		%	%	%
5 lbs.	5 lbs. 9.1/2 ozs.	78.2	69.2	99.0
5 lbs.	5 lbs. 8.1/4 ozs.	78.2	70.58	99.6
5 lbs.	5 lbs.10.1/2 ozs.	78.2	68.47	99.1

2.3. The results of table I show that 99% of the uranium in the crude sodium diuranate is recovered in the form of the peroxy complex.

3. Composition of the peroxy complex fluorides of uranium:

3.1. The peroxy-complex fluorides of uranium have been represented by the general formula $M_4U_4O_{15}F_6.XH_2O$ where M = K,NH_4,1/2 Ba and it is reported in literature that the formulae of these compounds are not difinitely established. An attempt was therefore made to ascertain the exact composition of these compounds. Lordkipanidze[16] has given the formula $K_4U_4O_{15}F_6.4\ H_2O$ for the potassium form of the peroxy-complex. In this laboratory both the potassium and ammonium forms of the complex were prepared in a pure state and were analysed chemically. To a solution of pure uranyl nitrate obtained by solvent extraction of crude uranyl nitrate with diethyl ether, enough ammonium or potassium fluoride was added to complex all the uranium present in solution and the peroxy-complex was precipitated by the addition of hydrogen peroxide followed by ammonia or potassium hydroxide to adjust the pH to 6. The precipitate was washed with 1% ammonium nitrate solution till the filtrate was free from fluoride ions. The precipitate was then washed with dilute hydrochloric acid (N/1000) till all the NH_4^+ or the K^+ ions were removed and finally with distilled water to remove the last traces of chloride. The precipitate was then dried in a desiccator to constant weight. The ammonium salt was then analysed for ammonia, peroxy oxygen, uranium and fluorine and the potassium salt for peroxy oxygen, uranium and fluorine. The results of the chemical analysis are given in table II.

Table II

Analysis of ammonium and potassium peroxy fluorides of uranium

Sample	Constituent				Atomic ratios			
	NH_4 %	O^* %	U %	F %	NH_4	: O^*	: U	: F
1. Ammonium uranium peroxy fluoride	3.47	4.07	65.56	3.82	0.7	: 0.92	: 1	: 0.73
2. Potassium uranium peroxy fluoride	-	3.33	63.93	7.79	-	: 0.78	: 1	: 1.526

* peroxy oxygen

3.2. The results of table II show that while in the potassium salt the U:F corresponds to the ratio 1:1.5 in agreement with the general formula $M_4U_4O_{15}F_6.XH_2O$ as reported in literature, in the case of the ammonium salt the ratio of U:F is 1:0.73. From the atomic ratios the ammonium salt can be represented empirically by the formula $3NH_4F.4\ UO_4$. On the basis of this formula equation 5, in the case of the ammonium compound, can be re-written as

$$4(NH_4)_3UO_2F_5 + 4\,H_2O_2 + 8\,NH_4OH \longrightarrow (NH_4)_3U_4O_{16}F_3 + 17\,NH_4F + 8\,H_2O \qquad (6)$$

Further studies on the identity of this compound are still being carried out.

4. Reaction between ammonium uranium peroxy fluoride and freon-12:

4.1. Materials used: (a) Freon-12 or dichlorodifluoromethane.

(b) Ammonium uranium peroxy fluoride, prepared as described previously and having a sieve analysis as in table III and a U_3O_8 content of 69.9%.

Table III

Sieve analysis of the peroxy fluoride

Mesh size	Percent material	Mesh size	Percent material
+ 10	13.63	-60, + 100	9.23
-10, + 20	26.95	-100, + 200	10.88
-20, + 30	24.73	-200	8.68
-30, + 60	5.90		

4.2. Apparatus and Procedure:-

The apparatus used for the reaction of ammonium uranium peroxy fluoride with freon-12 is shown in fig.4. It consisted of the reaction tube 'B', 36" long and 2" diameter, made of pyrex glass, and a nichrome wound electric tube furnace 'A'. The tube 'B' had a constriction at 'C' to support the perforated graphite disc 'D' on which the charge 'E' was placed. The temperature of the furnace was measured by means of a calibrated chromel-alumel thermocouple 'F' placed close to the reaction zone in conjunction with a previously calibrated millivoltmeter 'G'. Freon-12 from the cylinder was dried by passing the gas through the sulphuric acid bubbler 'H'. The rate of passage of gas was measured by the calibrated sulphuric acid flowmeter 'I'. The gaseous products of the reaction were passed through the receiver 'J' where some of the volatiles condensed and then through a wash bottle containing sodium hydroxide. The uncondensed and unabsorbed gaseous products were let out to the atmosphere.

4.3. To begin with, the charge was gradually heated in a current of nitrogen. The volatiles (H_2O etc.) liberated during this period were driven off into the receiver by playing a hot flame over the cold end of the reaction tube. When the charge attained the desired temperature, nitrogen was replaced by freon-12. The rate of passage of gas was adjusted to the required value and the reaction was carried out for a known time interval. $FeCl_3$, $ZrCl_4$, etc., formed during the reaction were condensed in the receiver.

At the end of the reaction the supply of freon-12 was stopped and the charge was allowed to cool. The green crystals of UF_4 were removed from the reaction tube and were washed with water free from the chlorides formed during the reaction. The crystals were then dried at 110°C and weighed.

4.4. Influence of temperature:

The influence of temperature on the reaction between ammonium uranium peroxy fluoride and freon-12 is given in table IV.

Table IV

Effect of temperature on the yield of UF_4

Weight of the charge - 225 gms.
Bed height - 7.0 cms.
Freon rate - 6.25 litres/hr. (Volume at room temp. and atmospheric pressure).
Time of reaction - 4 hours

Temperature °C	Yield of UF_4 gms.	Percent yield of UF_4	Remarks
350	-	-	No reaction
400	-	-	No reaction
450	165	93.1	-
500	167	94.2	-

4.5. The results in table IV show that the freon reaction is initiated between 400°C and 450°C and more than 90% UF_4 is formed at 450°C and above.

4.6. Influence of freon rate:

The effect of rate of passage of freon-12 on its reaction with ammonium uranium peroxy fluoride was studied at 500°C and the results are given in table V.

Table V

Effect of freon rate on the yield of UF_4

Weight of the charge	- 225 gms.
Bed height	- 7.0 cms.
Temperature of the reaction	- 500°C
Total amount of freon passed	- 25 litres (at room temperature and atmospheric pressure)

Rate of freon(litres/hr.)	Yield of UF_4	Percent yield of UF_4
12.50	156.0	88.0
10.00	164.0	92.5
8.33	165.0	93.1
6.25	167.0	94.2
5.00	170.0	96.0

4.7. The results of table V indicate that the yield of UF_4 increases by carrying out the reaction over a longer period in a slow current of freon. For 225 gms. of the charge occupying a bed height of 2.75" the rate of freon should be $\leqslant$ 10 litres/hr. to get higher than 90% yields of UF_4

4.8. Influence of the quantity of freon:

The effect of varying the amount of freon on the yield of UF_4 was studied at 500°C and the results are given in table VI.

Table VI

Effect of varying the quantity of freon on the yield of UF_4

Weight of the charge	- 225 gms.
Bed height	- 7.0 cms.
Temperature of the reaction	- 500°C
Time of reaction	- 4 hours

Total amount of freon passed (litres) at room temp. and atmospheric pressue	Yield of UF_4 (gms)	Percent yield of UF_4
15.7	120.0	67.7
18.8	141.0	79.6
21.9	155.0	87.5
25.0	167.0	94.2
30.0	168.0	94.8

4.9. The results in table VI show that for a charge of 225 gms, increasing the freon beyond 25 litres did not increase the yield of UF_4 appreciably.

4.10. Effect of particle size:

The particle size of ammonium uranium peroxy fluoride was varied from +10 mesh to -100, +200 mesh and the reaction was carried out at 500°C with freon-12 for 4 hours. The results of these experiments are given in table VII.

Table VII

Effect of particle size on the yield of UF_4

Weight of the charge - 225 gms.
Bed height - 7.0 cms.
Temperature of the reaction - 500°C
Time of reaction - 4 hours
Freon rate - 6.25 litres/hr.

Particle size (mesh)	Yield of UF_4 (gms.)	Percent yield of UF_4	Remarks
-4, + 10	172.0	97.0	-
-10, + 20	165.0	93.0	-
-20, + 30	150.0	84.7	-
-100, +200	-	-	Incomplete reaction
As in table III	167.0	94.2	-

4.11. The results of table VII show that the yield of UF_4 increases with the coarseness of the material upto 10 mesh tried here. This was essentially due to the partial clogging which occurred when finer sizes were present.

4.12. Based on the above data a few experiments were carried out with various amounts of the charge and the results are given in table VIII. The experiments with charge upto 900 gms were carried out in a pyrex glass tube of 2" diameter and those with 2250 gms in a tube of 3" diameter.

Table VIII

Yield of UF_4 with various amounts of the charge

Weight of the charge (gms.)	Time of reaction (hours)	Rate of freon (litres/hr)	Bed height (cms.)	Yield of UF_4 gms.	Percent
225	5	5	7.0	170.0	95.9
450	5	10	12.5	340.0	95.9
900	5	20	22.5	670.0	94.5
2250	6	42	44.0	1680.0	94.8

5. Nature of uranium tetrafluoride:

5.1. Purity:- The uranium tetrafluoride prepared as described above and dried at 110°C was still found to contain some moisture which could be removed by heating it to 300°C in a current of air or nitrogen. The average moisture content of the final sample was found to be 0.6-0.7%.

5.2. The analysis of crude sodium diuranate, ammonium uranyl fluoride liquor, ammonium uranium peroxy fluoride and uranium tetrafluoride are given in tables IX, X and XI.

Table IX

Analysis of sodium diuranate

Constituent	Percent	Constituent	Percent
U_3O_8	78.20	Alkalis	7.80
Rare earth oxides	1.77	Silica	0.62
ThO_2	0.65	P_2O_5	0.15
Fe_2O_3	0.55	Chlorides	0.01
ZrO_2	0.38	Loss on ignition	4.70
Al_2O_3 + TiO_2	2.22		
CaO	1.41		
MgO	0.38		

Table X

Analysis of ammonium uranyl fluoride liquor and ammonium uranium peroxy fluoride for some important constituents

Constituent	Ammonium uranyl fluoride liquor	Ammonium uranium peroxy fluoride
Uranium	40.23 gms/litre	59.85 %
Fe_2O_3	0.12 "	0.17 %
SiO_2	0.14 ""	0.13 %
ThO_2	10-20 ppm (U_3O_8 basis)	2-3 ppm
Cerium	< 3.0 " "	< 3.0 "
Gadolinium	< 0.5 " "	< 0.5 "
Samarium	< 0.25 " "	< 0.25 "
Dysprosium	< 0.5 " "	< 0.5 "
Erbium	< 0.5 " "	< 0.5 "
Europium	< 0.5 " "	< 0.5 "

Table XI

Analysis of uranium tetrafluoride

Constituent	Method of analysis	Amount present in the sample dried at 110°C
Uranium	Chemical	74.28 %
Fluorine	-do-	23.72 %
Moisture	-do-	0.69
Silica	-do-	0.13 %
UO_2F_2	-do-	1.43 %
CaO	-do-	0.02 %
MgO	-do-	0.04 %
Fe	-do-	146 ppm
ThO_2	-do-	5.3 ppm
Ce	Spectrographic	1.7 ppm
Sm	-do-	< 0.1 ppm
Gd	-do-	0.06 ppm
Dy	-do-	< 0.1 ppm
Er	-do-	< 0.05 ppm
Eu	-do-	< 0.05 ppm
Cd	Chemical and Spectrographic	0.065 ppm
Boron	Spectrographic	1.0 ppm
Copper	-do-	5.0 ppm
Nickel	-do-	< 1.0 ppm
Beryllium	-do-	< 1.0 ppm
Vanadium	-do-	< 1.0 ppm
Tin	-do-	< 1.0 ppm
Lead	-do-	< 1.0 ppm
Chromium	-do-	< 5.0 ppm
Antimony	-do-	< 2.0 ppm
Zinc	-do-	< 20 ppm
Aluminium	-do-	About 50 ppm
Manganese	-do-	2.0 ppm
Sodium	-do-	About 200 ppm

(All the spectrographic analyses were carried out on the U_3O_8 obtained by igniting UF_4 at 1000°C)

5.3. X-ray analysis:

The uranium tetrafluoride prepared by the freon reaction was emerald green and had a crystalline appearance. Single crystal and x-ray powder diffraction data of the sample have been studied in this laboratory by Jagdish Shankar et al[16] and their values for the cell dimensions and refractive indices of the sample are given below:

Cell dimensions:- $a = 12.73\ \mathring{A}$, $b = 10.75\ \mathring{A}$, $c = 8.43\ \mathring{A}$

$$\beta = 126^\circ\ 20'$$

Refractive indices:-

$$\alpha = 1.5000 \pm 0.004, \quad \beta = 1.584 \pm 0.004, \quad \gamma = 1.596 \pm 0.004$$

These values agree well with Zachariasen's[19] values for UF_4 obtained by vacuum distillation at 1000°C.

5.4. Packing density:- The packing density of the UF_4 (dried at 110°C) was determined by the ASTM method[20] and was found to be 3.23 gms/c.c. On heating in vacuum at 650°C the material was found to sinter but there was no appreciable change in packing density.

6. Discussion:

6.1. The precipitation of rare earths as fluorides has been recognised as one of the classical methods of its separation from many other elements[21]. Starting from crude sodium diuranate containing uranium and rare earths in the ratio 40:1 the rare earths could be reduced to a value less than 5 ppm using ammonium fluoride. The fact that this small amount of rare earths still remain in solution may be due to the solvent effect of uranium upon rare earth fluorides as reported by Short and Dutton[22]. Studies on the preparation of ammonium uranium peroxy fluoride showed that 99% of the uranium present in the diuranate could be recovered in the form of the complex.

6.2. The filtration characteristics of the thorium and rare earth fluorides and ammonium uranium peroxy fluoride (Fig.3 and Fig.4) show that the two slurries can be filtered without difficulty. However it would be advantageous to filter them after they are partly settled as this would reduce the total time required for the operation.

6.3. The reaction between ammonium uranium peroxy fluoride and freon-12 starts between 400°C and 450°C and even at 450°C the yield of UF_4 is more than 90%. The slower the rate of passage of gas the greater is the yield of UF_4. At higher flow rates of freon the amount of chlorides formed are greater. The reaction between uranium trioxide and freon-12 has been represented by Booth et al by the equation

$$UO_3 + 2\,CCl_2F_2 \longrightarrow UF_4 + COCl_2 + CO_2 + Cl_2 \qquad \text{-- (7)}$$

Ammonium uranium peroxy fluoride on heating in nitrogen at 400°C loses ammonia, peroxidic oxygen and water vapour. So its reaction with freon-12 can be represented empirically by the equation

$$3\ NH_4F.4\ UO_4 + 13/2\ CCl_2F_2 \longrightarrow 4\ UF_4 + 3\ NH_3 + 2O_2 + 4\ CO_2 + 4\ Cl_2 + 5/2\ COCl_2 + 3/2\ H_2O \qquad \text{-- (8)}$$

The experiments with varying amounts of freon show that the reaction does not take place stoichiometrically according to the equation 8 as the quantity of freon-12 required to get more than 90% yields of UF_4 is 8 moles per mole of the peroxy complex. The formation of the chlorides of uranium together with UF_4 may be due to some side reactions, for example with the phosgene which is a product of the reaction.

6.4. The variation in particle size of the ammonium uranium peroxy fluoride showed a decrease in the yield of UF_4 with the fineness of the material. This is due to the caking tendency of the charge, apparently due to the chloride formation, a tendency which increased with the fineness of the particle. Sometimes due to the caking of the charge, the pores of the perforated disc were choked and further reaction was hindered. However with a charge containing a mixture of various sized particles as given in table III the yield of UF_4 was as high as 94%.

6.5. For ordinary purposes, the uranium tetrafluoride prepared by the above method is sufficiently pure but it still contains some impurities which are not within the limits for a nuclear grade material. The chief impurity amongst these is boron which could probably be got rid of by using nuclear grade graphite-lined reaction tubes. The packing density of the material is in the range required for its use in preparing uranium metal by magnesium reduction. Attempts to reduce further the impurities present in the UF_4 namely silica, iron, sodium, etc., are in progress.

PART II

7. Preparation of uranium tetrafluoride by photochemical reduction

(In collaboration with Mr T.R.Bhat)

7.1. It was first observed by Bucholz[23] that aqueous solutions of uranyl nitrate and uranyl sulphate could be reduced photochemically in sunlight in presence of an organic reducing agent. Bolton prepared potassium uranium fluoride by this method using formic acid as reducing agent. In recent years Ivan Gal[2] has made a detailed study of the photo-reduction of uranyl nitrate solution in presence of alcohol to get uranium tetrafluoride.

7.2. In countries where the weather conditions vary much the use of a photochemical method loses its significance. But in a country like India, where sunlight is abundant most of the year, such a method would acquire importance. Moreover the specificity of the photochemical reaction and the cheap availability of the raw materials are factors which favour the preparation of pure uranium tetrafluoride by this method.

7.3. In this laboratory preliminary investigations have been carried out on the photochemical reduction of ammonium uranyl fluoride solution to get ammonium uranium fluoride which is subsequently decomposed to uranium tetrafluoride. Starting from crude sodium diuranate ammonium uranyl fluoride solution was prepared as described in part I. The optimum conditions for the preparation of ammonium uranium fluoride by photochemical reduction were investigated and the results are given below:

7.4. 100 c.c. of ammonium uranyl fluoride solution containing about 3.7 gms U was exposed to sunlight in pyrex beakers in presence of various reducing agents and the results are given in table XII.

Table XII

Effect of various reducing agents on the photochemical yields of NH_4UF_5

Reducing agent	Time of irradiation	Yield of uranium g	Yield of uranium %
1. Formic acid 1M	180 minutes	2.11	56.8
2. Ethanol 1M	"	2.04	54.9
3. Isopropyl alcohol 1M	"	1.51	40.7
4. Mandelic acid 1M	"	1.47	39.6
5. Acetone 1M	"	1.33	35.7
6. Glycerol 1M	"	1.18	31.8
7. Methanol 1M	"	0.94	25.4
8. Oxalic acid 1M	"	0.13	3.5

7.5. The results of the table XII show that formic acid and ethanol are the most suitable reducing agents.

7.6. The influence of various acids was next studied using alcohol and formic acid as reducing agents. It was observed that for maximum yields a combination of sulphuric acid and ethanol or acetic acid and formic acid were the best. Hydrochloric acid inhibited the reaction to a large extent. The nature of the ammonium uranium fluoride formed varied in the two cases and a denser material was obtained using ethanol-sulphuric acid mixtures. From a solution containing 3.7 gms. U/100 c.c. and using 10-13% alcohol and 1% H_2SO_4 the yield of ammonium uranium fluoride was 90-95% in 4 hours. The yield of the fluoride per unit area depends on the height of the liquid column and hence the effect of this variable was next investigated. The results are given in Fig.5. From the curves in Fig.5 it is seen that the optimum depth for a solution containing 4.8% U, 10% alcohol and 1% H_2SO_4 is 7.5". Spectrophotometric measurements showed that this mixture had a maximum absorption at 420 mμ and by using different filters it was noticed that 95% of the photochemical reaction took place in the blue region of the visible spectrum.

7.7. The decomposition of ammonium uranium fluoride to get uranium tetrafluoride has been previously investigated by Leah et al and others[24,25]. In Belgium, ammonium uranium fluoride is prepared by the reaction of UO_2 with NH_4HF_2 and it is then decomposed to UF_4 by heating in vacuum. The optimum conditions for the vacuum decomposition of NH_4UF_5 as observed here are given in Fig.6. The uranium tetrafluoride obtained by this method was found to have a packing density of 1.6 gms/c.c. On heating the sample in vacuum to a higher temperature the packing density of the material altered enormously. The sintering of UF_4 starts above 600°C. The effect of temperature on the packing density of UF_4 is given in Fig.7.

7.8. Using the best conditions, the preparation of pure uranium tetrafluoride of high packing density is being carried out on a larger scale. The degree of purity of the product is being ascertained.

8. Acknowledgement:

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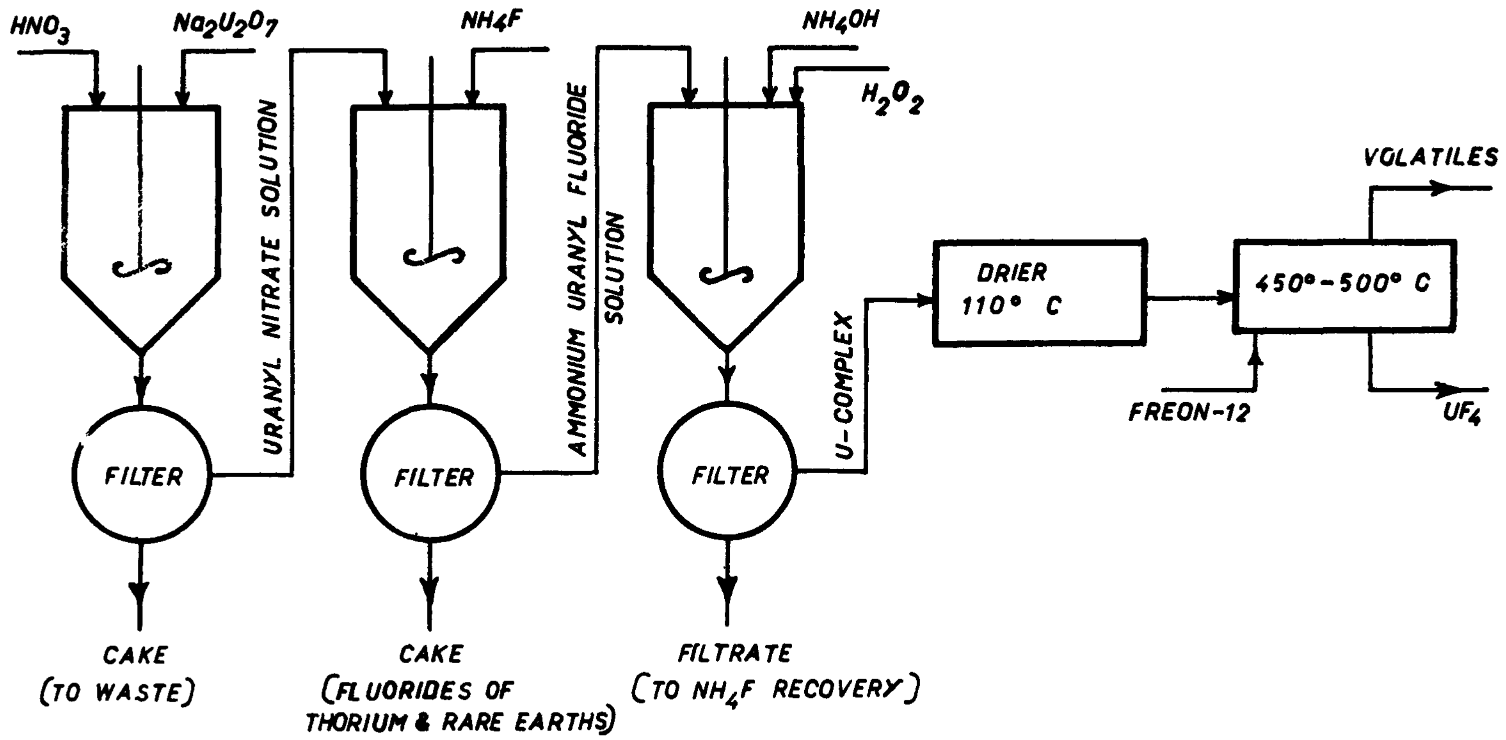
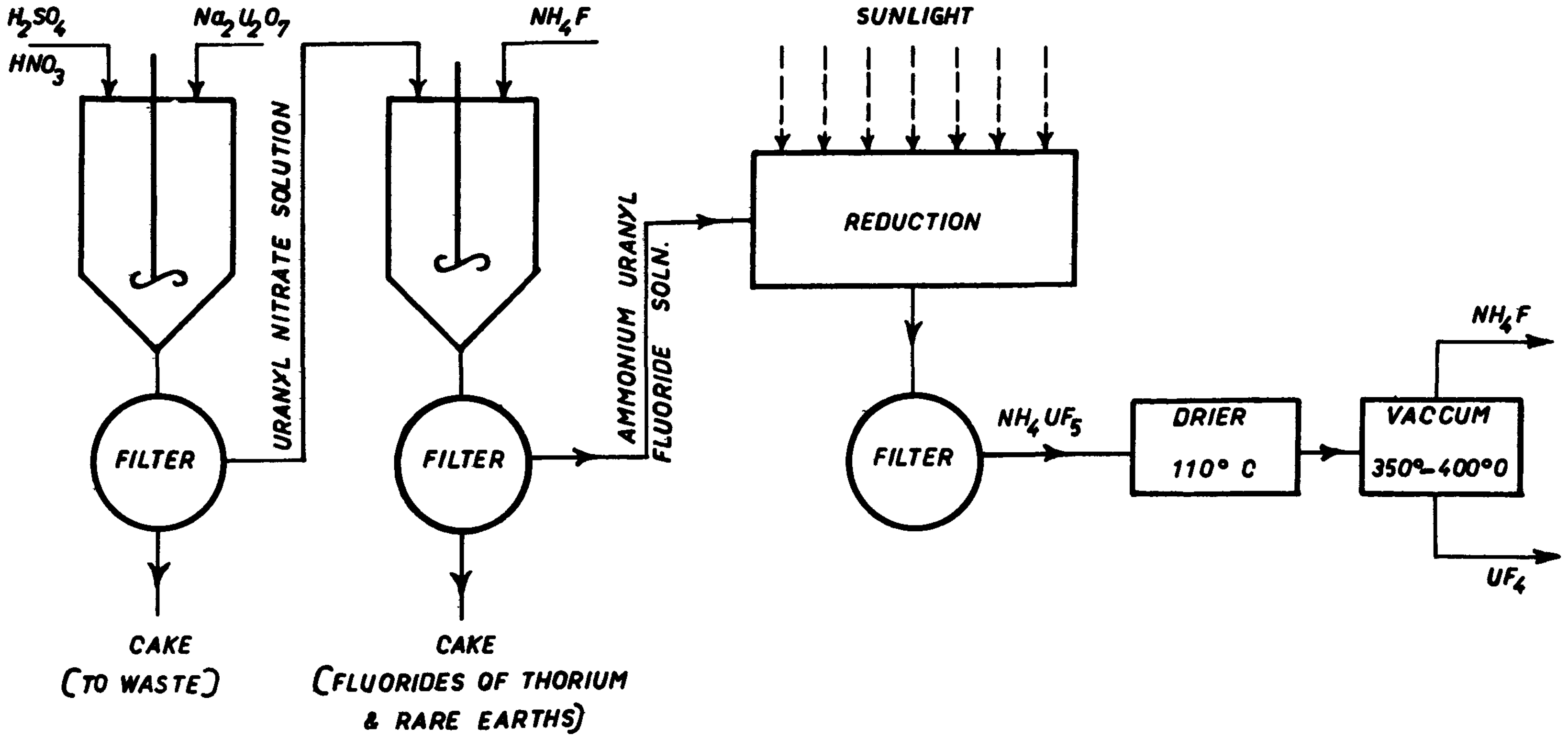
FIG.1 (a)



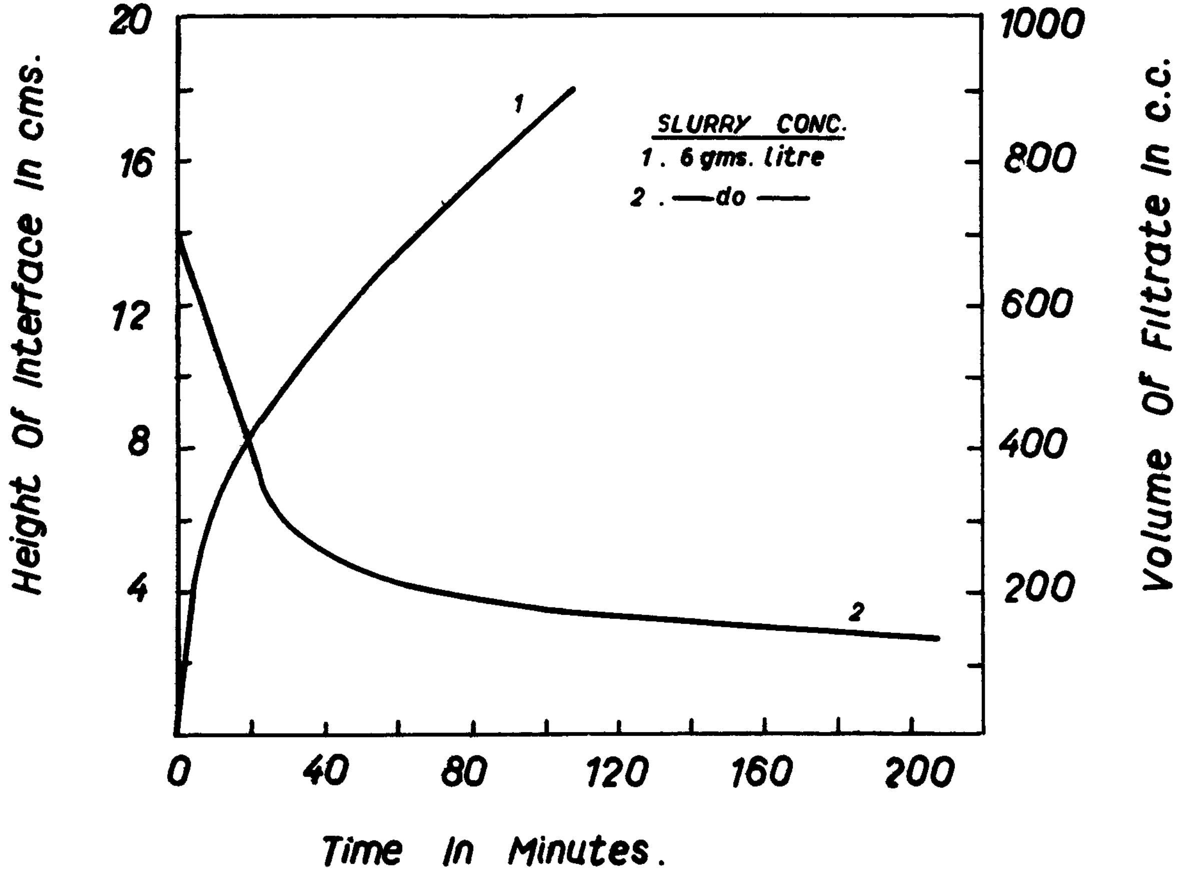
FLOW SHEET FOR PREPARATION OF UF_4 USING FREON-12

FIG.1 (b)



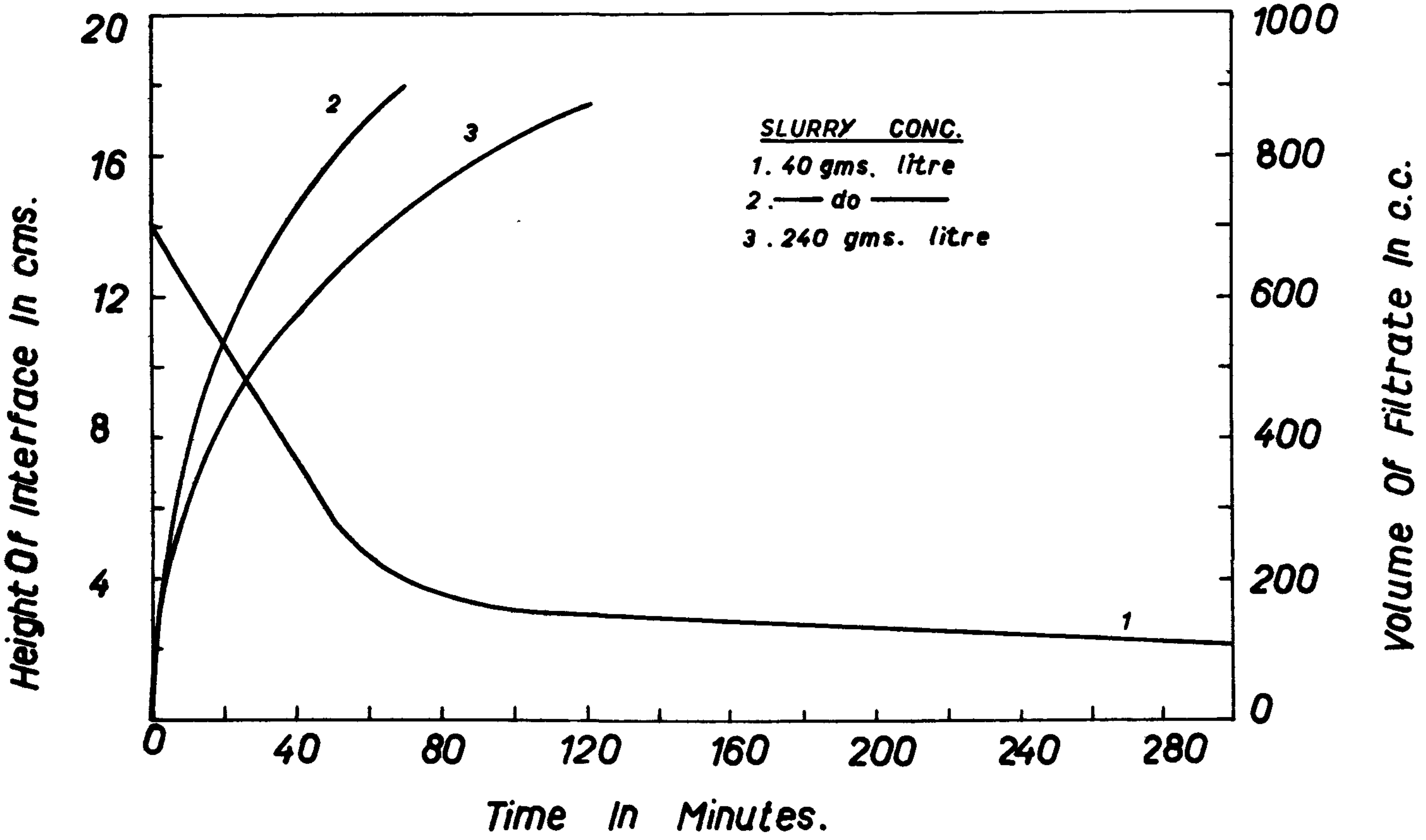
FLOW SHEET FOR THE PREPARATION OF UF_4 BY PHOTOCHEMICAL REDUCTION

FIG.2



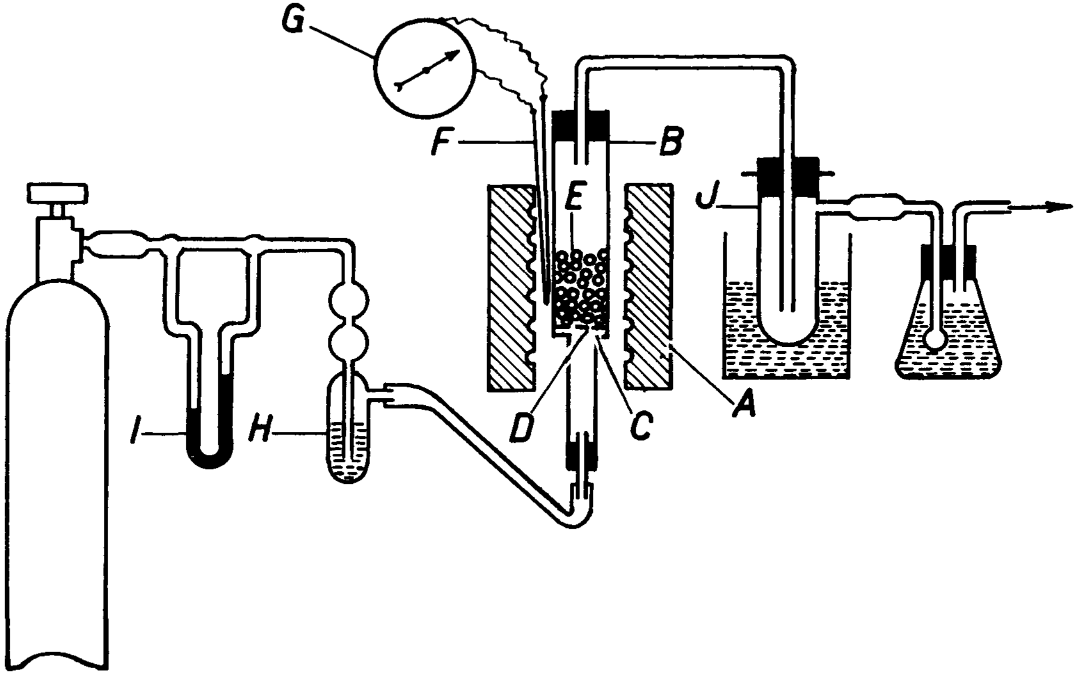
RATES OF SETTLING & FILTRATION OF THORIUM & RARE EARTHS FLUORIDES

FIG. 3



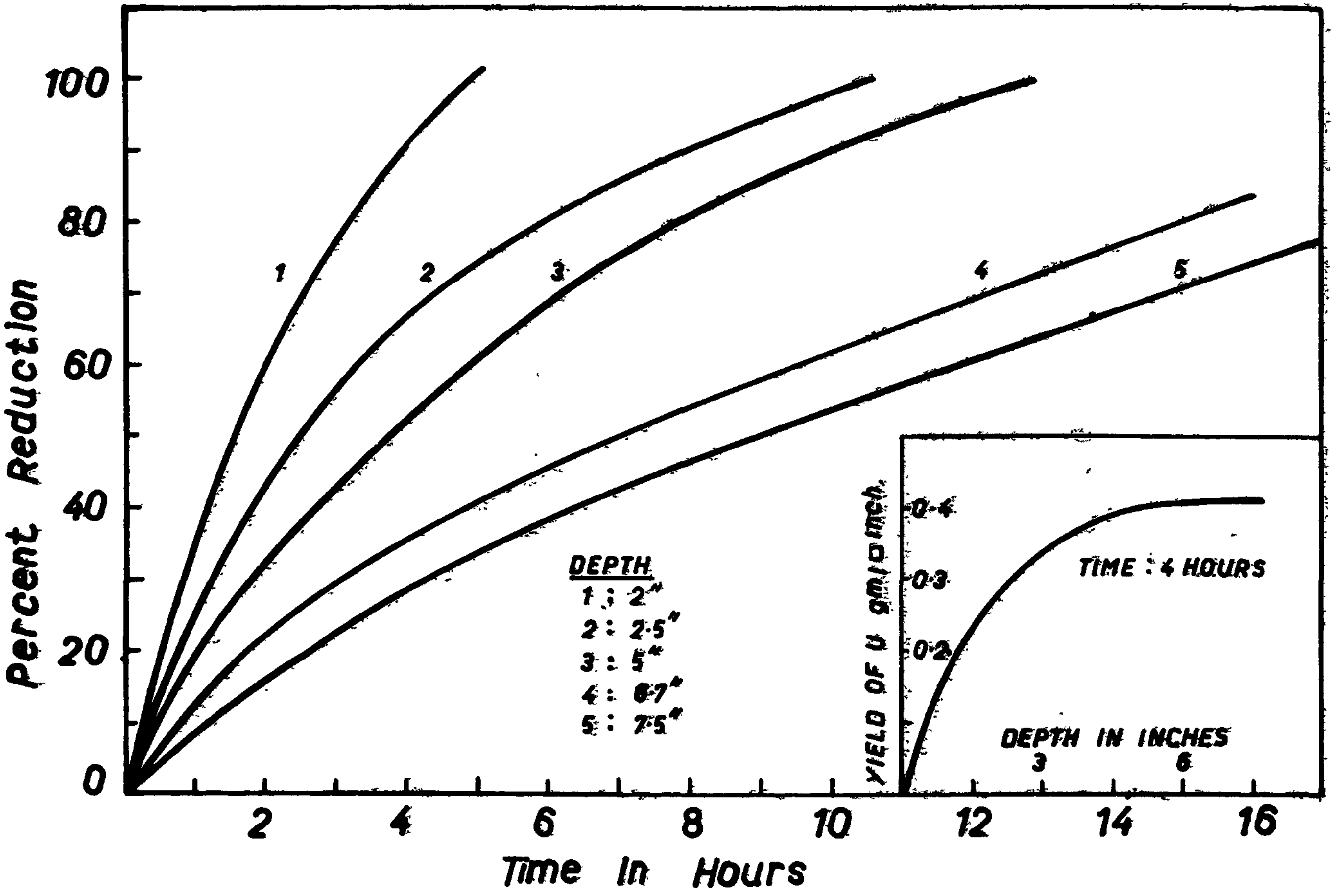
RATES OF SETTLING & FILTRATION OF AMMONIUM URANIUM PEROXY FLUORIDE

FIG. 4



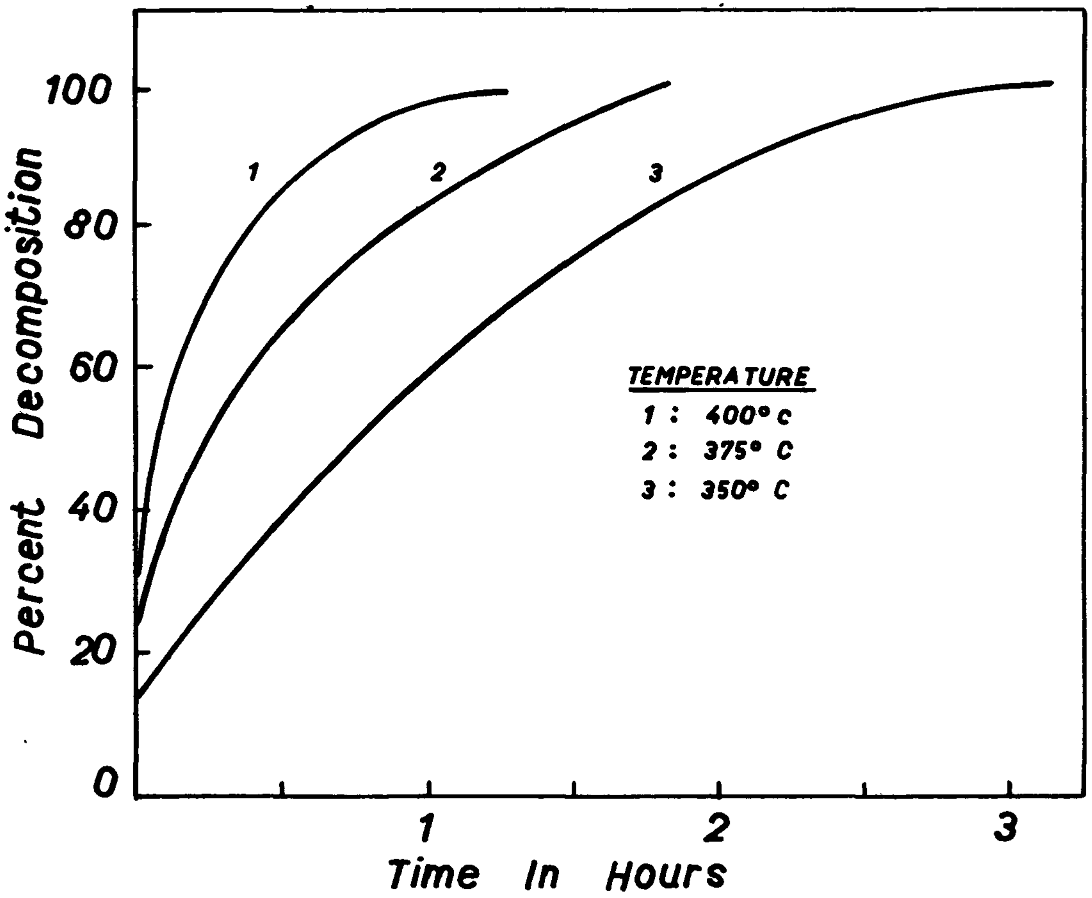
APPARATUS FOR THE PREPARATION OF URANIUM TETRA FLUORIDE

FIG. 5



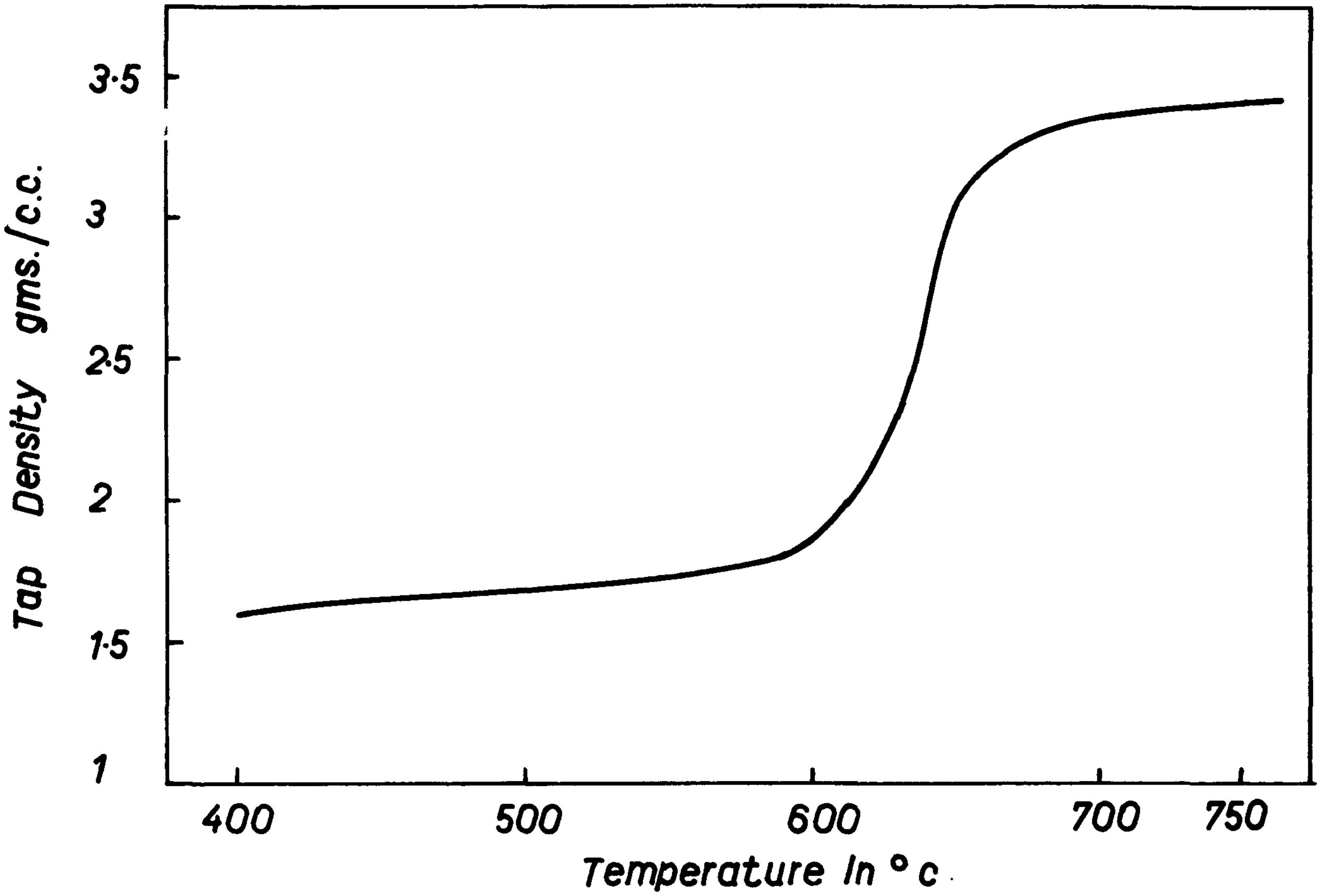
VARIATION OF PERCENTAGE CONVERSION WITH DEPTH OF SOLUTION

FIG. 6



ISOTHERMAL DECOMPOSITION OF NH_4UF_5

FIG. 7



EFFECT OF TEMPERATURE ON TAP DENSITY OF UF_4