ELECTROLYTIC PREPARATION OF UF_4

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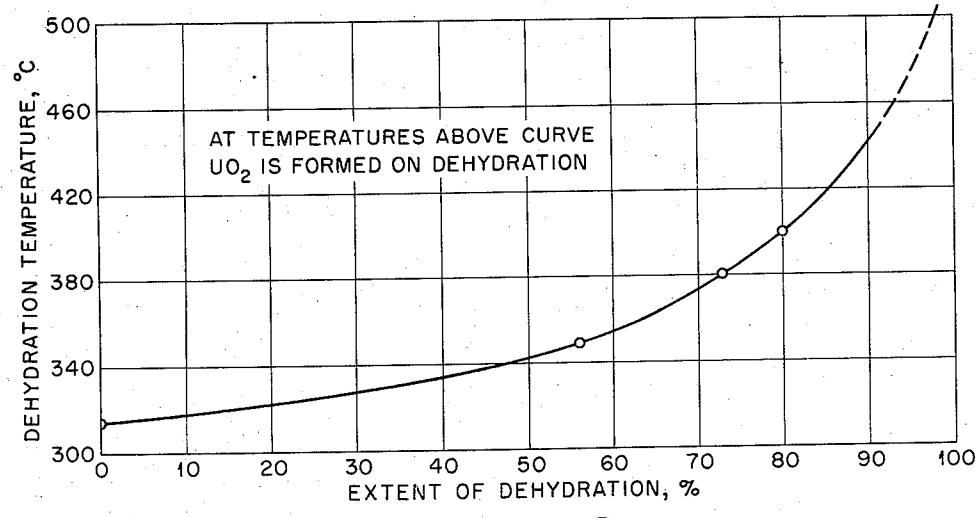


Fig. 2.

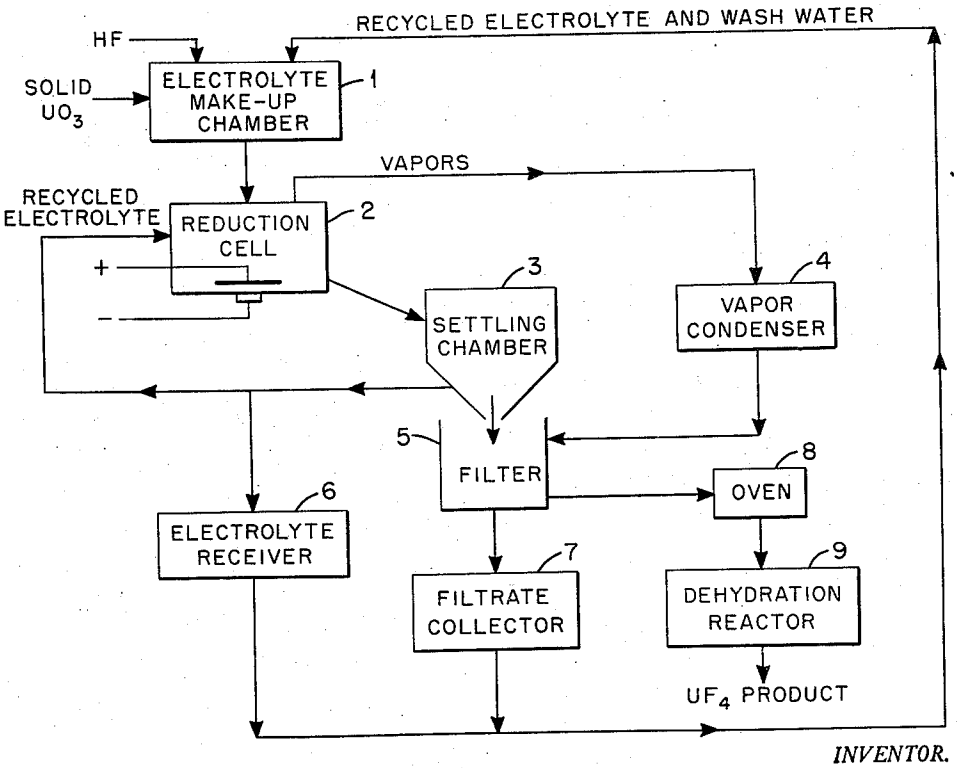


Fig. 1.

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ELECTROLYTIC PREPARATION OF UF_4

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6 Claims. (Cl. 204—1.5)

Our invention relates to an improved electrolytic method for the preparation of uranium tetrafluoride.

Uranium tetrafluoride has been prepared by electrolytic reduction of uranyl ions and simultaneous reaction of the reduced ions with hydrofluoric acid in an electrolytic cell at temperatures up to approximately 35° C. The product of this reaction is a hydrate represented by the formula $UF_4 \cdot 2.5H_2O$. The disadvantages associated with this hydrate have made the electrolytic production of uranium tetrafluoride impractical. This hydrate is voluminous and difficult to handle in the continuous operation of an electrolytic cell. The hydrate settles slowly and after filtration requires washing with large amounts of water to remove hexavalent uranium. Recycling this large volume of hexavalent uranium-containing wash water reduces the electrolyte concentration, causing low current efficiency and fluctuating power consumption. In addition $UF_4 \cdot 2.5H_2O$ upon dehydration at elevated temperatures oxidizes excessively to hexavalent uranium and UO_2.

It is, therefore, an object of our invention to provide an electrolytic method for the preparation of uranium tetrafluoride in which a high-density hydrate is formed in the electrolytic cell.

Another object is to provide a continuous electrolytic method for the preparation of uranium tetrafluoride.

Another object is to provide an electrolytic method for the preparation of uranium tetrafluoride in which the presence of hexavalent uranium in the cell product is minimized.

Another object is to provide an electrolytic method for the preparation of uranium tetrafluoride in which oxidation of the uranium during dehydration is minimized.

Another object is to provide an electrolytic method for the preparation of uranium tetrafluoride in which the consumption of power in the electrolytic cell is relatively constant.

In accordance with our invention a solution containing uranyl ions is subjected to electrolytic reduction in the presence of hydrofluoric acid at a temperature of about 90 to 100° C. The resulting hydrate is separated from the electrolyte and dehydrated. We have found that by maintaining the cell temperature at about 90 to 100° C. a hydrate represented by the formula $UF_4 \cdot 0.75H_2O$ is formed. The properties of this hydrate are such that continuous operation of the electrolytic cell is made feasible. The hydrate has a relatively high density; consequently it may be readily separated from the electrolyte by continuous circulation as a slurry through a settling chamber. Vapor produced in the cell may be condensed, employed for washing the hydrate and recycled, thus maintaining the system at a relatively constant volume. As a result of maintaining this constant volume and continuously replacing the expended reagents, fluctuations in power consumption are minimized. Dehydration of the $UF_4 \cdot 0.75H_2O$ hydrate is accomplished without the formation of hexavalent uranium

or UO_2. The resulting product is finely divided, high purity uranium tetrafluoride.

The uranyl ions to be reduced by our invention are preferably supplied in the form of uranyl fluoride. Uranyl fluoride may be readily prepared by dissolving uranium trioxide in excess hydrofluoric acid. Although increased production rates may be obtained by the addition of mineral acids to the electrolyte, we prefer to employ only a solution of uranyl fluoride and hydrofluoric acid in order to minimize corrosion problems. The concentrations of UO_2F_2 and HF employed in the electrolyte are not critical to our invention. While concentrations of UO_2F_2 from 0.1 to 1.0 M may be used, we prefer concentrations from 0.2 to 0.5 because of the high current efficiencies obtained in this range. HF concentrations from stoichiometric with respect to UO_2F_2 to 200% excess may be employed, but we prefer from 50 to 100% excess.

Because of the reactivity of the electrolyte, corrosion-resistant materials are required for the construction of the cell. The body of the cell is preferably lined with a plastic resistant to HF. Equipment in contact with the electrolyte may also be protected by coating with a suitable enamel. The electrodes must resist corrosion and in addition support high current densities with high current efficiencies. Platinum is preferred for the anode, although other corrosion resistant metals may be employed within the scope of our invention. Solid metal cathodes present difficulty in that the UF_4 tends to coat on the cathode, increasing electrical resistance and lowering current efficiency. This difficulty is overcome by the use of a mercury cathode and by constant agitation of the electrolyte.

Operation of the electrolytic cell is affected by numerous variables, including temperature, concentration of reactants, cell product in the electrolyte and current density. As indicated above, a temperature of 90° C. or above is essential to our invention. For continuous cell operation it is preferred to maintain the electrolyte at approximately its boiling point. This temperature may be obtained by heating the cell with steam circulated through the anode. Electrolyte concentrations are maintained at the optimum levels referred to above. The amount of cell product solids present in the electrolyte in slurry form has a marked effect on current efficiency in the cell. We have found that at constant concentrations, temperature and electrode spacing a current efficiency of 85% is obtained at an electrolyte slurry density of 0.05 gram hydrate per cubic centimeter of electrolyte and at densities of 0.10 and 0.30 current efficiencies are lowered to 70 and 20 percent respectively. Accordingly, it is preferred to maintain the slurry level at about 0.05 by circulating the electrolyte through a settling chamber to remove the hydrate. The current efficiency of the cell is increased with increasing current densities. Under constant cell conditions current efficiency was increased from 77 percent at a cathode current density of 0.4 amp./sq. in. of cathode surface to 89% percent at 1.3 amp./sq. in. At the optimum electrolyte concentrations referred to above we have found 1.3 amp./sq. in. to be the maximum obtainable current density, this value being limited by the 0–12 volt, 0–60 amp. rectifier available to supply power to the cell. Although current density is not critical to our invention we prefer to use the maximum obtainable. The cell operates satisfactorily at voltages from 3 to 7.5 and current densities from 0.2 to 1.3 amp./sq. in.

Although the arrangement of the cell is not critical to our invention, we prefer to dispose the mercury cathode in the form of a pool at the bottom of the cell and suspend the platinum anode in the form of a coil about

one inch above the mercury. In order to maintain current efficiency a conventional stirring blade is suspended between the electrodes and rotated at about 120 R. P. M.

A preferred embodiment of our invention in a continuous cell may be explained by reference to Fig. 1. Electrolyte is prepared in a make-up chamber **1** by the dissolution of UO_3 in HF, and the electrolyte concentration is adjusted to the desired level. The electrolyte is introduced into an electrolytic cell **2** having a mercury cathode and a platinum anode. The hydrate which forms upon electrolysis is continuously circulated through a settling chamber **3**. The hydrate settles to the bottom and the effluent electrolyte is recycled to a receiver **6** and to the cell **2**. Vapors formed in the cell are circulated to a condenser **4** and the resultant liquid employed to wash the hydrate in a filter **5**. The settled hydrate is filtered and washed, and the filtrate is collected in a collector 7. The filtrate is recycled from the collector to the make-up chamber **1**. The resultant filter cake is then dried in an oven **8** and dehydrated in a high temperature dehydration reactor **9**.

Although the hydrate formed in the cell may be separated from the electrolyte by any conventional means, we prefer to circulate the electrolyte slurry through a settling chamber in which the hydrate is collected at the bottom. For maximum separation the settling chamber is of inverted conical shape, with a vertical baffle in the center. The slurry is introduced near the top of the chamber at an angle of about 30 degrees from the horizontal, circulated between the baffle and chamber wall, and removed by means of an outlet at the top of the chamber and opposite the inlet. Separation of the hydrate from the electrolyte may be increased by controlling the rate of flow of the slurry. We have found that maximum separation is obtained when the slurry is flowing upward in the chamber at a velocity of 1½ to 2 cm./min. At velocities above 7 cm./min. only slight separation is obtained.

Further separation of the hydrate from the electrolyte may be effected by filtering the collected slurry in a conventional filtering operation. We prefer to use a vacuum filter in which the electrolyte is substantially removed from the hydrate, leaving a filter cake. The resulting filter cake contains small amounts of hexavalent uranium which may be removed by washing with water. In continuous operation of the cell, condensed cell vapors may be used to wash the filter cake and recycled to the cell, thus maintaining a relatively constant liquid volume in the system. We have found that maximum washing efficiency is obtained when the filter cakes are approximately one inch thick. For one inch cakes only 0.5 cc. wash water per gram of hydrate is required to remove the hexavalent uranium. The filter cake may, however, be formed and washed in various dimensions within the scope of our invention, with a greater volume of wash water being used.

Uranium tetrafluoride is recovered from the hydrate filter cake by heating the cake to remove both excess moisture and the water of hydration. We have found that the presence of excess moisture during dehydration favors oxidation of the uranium and consequently lowers the purity of the UF_4. Accordingly, we prefer to remove the excess moisture in a preliminary drying step before dehydration is carried out. Although our invention is not to be understood as so limited, optimum results may be obtained by drying the cake in an oven by means of circulating air heated to approximately 100° C. This temperature is employed to minimize the formation of hexavalent uranium. The formation rate at this temperature is higher than at lower temperatures, but the total amount of hexavalent uranium is kept to a minimum because of the shorter time required for drying. A drying period of 6 to 12 hours is required, depending on the thickness of the cake.

Dehydration of the dried $UF_4 \cdot 0.75H_2O$ must be carried out under carefully controlled conditions in order to prevent the formation of uranium dioxide. Since oxygen assists the formation of UO_2, the dehydration is carried out in the absence of air, preferably under a nitrogen atmosphere. We have found that the temperature at which UO_2 forms during dehydration increases with the extent of dehydration as shown in Fig. 2. By employing gradually increasing temperatures below the curve in Fig. 2, the dehydration may be completed in about thirty minutes without the formation of UO_2 or hexavalent uranium. We prefer to use a ribbon-flight type dehydration reactor provided with three temperature zones—200° C., 320° C. and 400° C. The hydrate is successively fed through the three reactor zones at rates of 8.9 to 18 gm./min. and retained in the reactor from 20 to 50 minutes.

The resulting UF_4 is substantially pure in finely divided powder form, with a tap density of approximately 2.7 g./cc. and a surface area of approximately 2.1 sq. m./g.

Since it is apparent that many variations, particularly in apparatus and procedure, are possible within the scope of our invention, the invention is not to be understood as limited except as provided in the appended claims. The following example further illustrates our invention.

EXAMPLE I

A 0.5 M uranyl fluoride-3.0 M hydrofluoric acid electrolyte was prepared by dissolving UO_3 in HF. 6500 ml. of this solution was added to an electrolytic cell and an inverted conical settling chamber. The cell had a mercury pool cathode and a platinum anode suspended as a coil one inch above the cathode. The cell was heated to 100° C. by circulating steam through the anode coil. Reduction was started by turning on and adjusting a D. C. current rectifier to reach the desired current density. As soon as reduction was started, feed from a 1.37 M UO_2F_2-4.22 M HF solution was continuously added to hold the electrolyte concentration at a constant level. Electrolyte was continuously circulated through the settling chamber where the hydrate was collected. The thickened hydrate slurry was removed from the settling chamber, filtered in a Buchner filter with a vacuum of 26 inches of mercury across the cake and washed with approximately 0.5 ml. of condensed cell vapors per gram of dry cake. Results of several runs using this procedure are illustrated by Table I:

Table I

SUMMARY OF CELL DATA

Run No.	Average Current Density, amp./sq. in.	Average Cell Voltage, volts	Current Efficiency, percent	Power Utilization, g. UF_4/watt-hr.	Production Rate, g. UF_4/hr./sq. in.	Operation Time, amp./hr.
1	0.516	3.58	76.8	1.26	2.31	650.6
2	0.401	3.34	[1] 87.4	1.53	2.04	256.2
3	0.413	3.30	76.9	1.35	1.85	524.4
4	0.400	3.39	76.4	1.32	1.78	788.0
5	0.998	6.15	[1] 88.5	0.842	5.15	158.7
6	0.997	6.21	80.9	0.762	4.70	255.1
7	1.31	7.20	89.6	0.729	6.85	462.2

[1] These current efficiencies were high because a fresh electrolyte was used, and the slurry density had not increased to the equilibrium value.

The product of the above runs was a hydrate filter cake suitable for drying and dehydration in accordance with our invention.

Having thus described our invention, we claim:

1. A method of converting hexavalent uranium to UF_4 which comprises subjecting uranyl ions to cathodic reduction at a temperature of at least approximately 90° C. in an electrolytic cell containing as electrolyte an aqueous solution of hydrofluoric acid, separating the resulting $UF_4 \cdot 0.75H_2O$ precipitate from the resultant supernatant liquid and heating said precipitant until substantially complete dehydration to UF_4 is effected.

2. A method of converting uranyl fluoride to UF_4 which comprises subjecting the uranyl fluoride to cathodic

reduction at a temperature of approximately 90° C. to 100° C. in an electrolytic cell containing as electrolyte an aqueous solution of excess hydrofluoric acid, separating the resulting $UF_4 \cdot 0.75H_2O$ precipitate from the resulting supernatant liquid and heating said precipitate until substantially complete dehydration to UF_4 is effected.

3. A method of converting uranyl fluoride to UF_4 which comprises subjecting the uranyl fluoride to cathodic reduction in an electrolytic cell containing as electrolyte an aqueous solution of excess hydrofluoric acid at approximately the boiling point of said electrolyte, separating and condensing the resulting vapors, separating the resulting $UF_4 \cdot 0.75H_2O$ precipitate from the resulting supernatant liquid, washing said separated precipitate with the liquid resulting from the condensation of said vapors adding the resulting wash liquid to said electrolyte, and heating the washed precipitate at temperatures below the formation temperature of UO_2 until substantially complete dehydration to UF_4 is effected.

4. A method of converting uranyl fluoride to UF_4 which comprises continuously subjecting the uranyl fluoride to cathodic reduction in an electrolytic cell containing as electrolyte an aqueous solution of excess hydrofluoric acid at approximately the boiling point of said electrolyte, separating and condensing the resulting vapors, continuously circulating said electrolyte through a settling chamber, removing the $UF_4 \cdot 0.75H_2O$ precipitate from the settling chamber, filtering and washing said removed precipitate with the liquid resulting from the condensation of said vapors, adding the resulting wash liquid to said electrolyte, adding UO_2F_2 and HF to said electrolyte, and heating the washed precipitate at temperatures below the formation temperature of UO_2 until substantially complete dehydration to UF_4 is effected.

5. A method of converting UO_3 to UF_4 which comprises dissolving UO_3 in excess aqueous hydrofluoric acid, disposing the resulting solution to form an electrolyte in an electrolytic cell, subjecting the hexavalent uranium in said electrolyte to cathodic reduction at a temperature of approximately 90° C. to 100° C., separating the resulting $UF_4 \cdot 0.75H_2O$ precipitate from the resulting supernatant liquid, washing said precipitate, and heating said washed precipitate until substantially complete dehydration to UF_4 is effected.

6. A method of converting UO_3 to UF_4 which comprises dissolving UO_3 in excess aqueous hydrofluoric acid, disposing the resulting solution to form an electrolyte in an electrolytic cell, subjecting the hexavalent uranium in said electrolyte to cathodic reduction at approximately the boiling point of said electrolyte, separating and condensing the resulting vapors, separating the resulting $UF_4 \cdot 0.75H_2O$ precipitate from the resulting supernatant liquid, washing said separated precipitate with the liquid resulting from the condensation of said vapors, adding the resulting wash liquid to said electrolyte, drying said washed precipitate, and heating said dried precipitate to temperatures below the formation temperature of UO_2 until substantially complete dehydration is effected.

No references cited.