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Short communication

Uranium tetrafluoride production using the dropping mercury electrode

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ABSTRACT

This work shows the technical feasibility to obtain uranium tetrafluoride through an electrochemical process using a dropping mercury electrode. This product was obtained from ammonium diuranate, dissolved in hydrofluoric solutions, using concentrations of 50 g/L UO₂F₂. The system was evaluated with current intensities densities from 1.6 to 6.3 A and temperatures from 25 to 65 °C. The maximum current efficiency achieved was 95 %. The UF₄ powders achieved spherical morphology, with diameters between 40–60 µm. This property allows correct compaction for the subsequent production of metallic uranium, which allows reaching high-density UF₄ – Mg mixtures, between 3.0–3.5 g/cm³, as it was proven in our previous studies. This technique achieved this result thanks to the electrochemical properties of the mercury, when used as cathode. The impurity levels of this product obtained by electrolysis are only those that come from the initial ammonium diuranate concentrates. This method is an alternative to the classic process of UF₄ precipitation in an aqueous medium using reducing agents, as the conventional stannous chloride (SnCl₂), which commonly contaminate uranium compounds.

1. Introduction

The nuclear fuel cycle is the set of associated activities to obtain electrical energy, based on nuclear power plants, or for the production of radiopharmaceuticals in research reactors. The tasks involved in the uranium production start with the extraction of uranium ore and subsequent acid leaching, either in milling operations or near mine sites [1, 2]. Once obtained a leaching solution, uranium is concentrated and purified through chemical purification processes, commonly solvent extraction or ionic exchange. A later precipitation stage provides uranium ore concentrates, usually ammonium diuranate (ADU), ammonium uranyl carbonate (AUC), triuranium octoxide (U₃O₈), or uranyl peroxide (UO_4) [3,4]. The next step is the production of gaseous UF₆ for uranium enrichment. Uranium must be enriched in its ²³⁵U isotope for nuclear fuel manufacture [5,6]. The enriched UF₆ must return to its previous UO₂ or UF₄ form. There are two paths to obtain uranium tetrafluoride [7]. The most usual process involves refining through aqueous reactions, often called the "wet process" [8]. The alternative route to UF₄ production includes conversion and later refinement from the previously obtained UF₆. Since no aqueous medium is present, this method is known as the "dry process" [9,10].

Uranium tetrafluoride is the starting product to obtain metallic uranium using Mg as reducing agent [12], either as raw material for nuclear fuels or the production of UF_6 for uranium enrichment. UF_4 is a

green crystalline solid and it is not soluble in water. The bulk density of the UF₄ powders ranges between 2.0–4.5 g/cm³. This outcome is a direct consequence of the compactness, given by nucleation and growth mechanisms involved in the UF₄ production [13]. UF₄ must contain at least 96 % of uranium tetrafluoride, due to the yield of the UO₂ conversion process. This product must be anhydrous and possess a high density during the refining process to yield metallic uranium. Table 1 shows the maximum impurity levels allowed for UF₄ production.

1.1. Production of UF₄ from UO₂ (dry process)

The calcined uranium concentrates (U₃O₈), react with hydrogen in an H₂-N₂ atmosphere, using a fluidized bed reactor, at temperatures between 500–800 °C, to give uranium dioxide (UO₂), with a yield of 99 % UO₂, according to the reaction (1) [15]:

$$U_3 O_8 + 2H_2 \to 3UO_2 + 2H_2 O \tag{1}$$

 UO_2 then goes into the hydrofluorination process to obtain UF_4 according to the reaction (2):

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O \tag{2}$$

The reactor for UF₄ production allows the application of HF gas into trays containing UO₂ spread uniformly to increase the active surface. This reaction takes place at temperatures of 485 ± 28 °C. Higher

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Table 1

Specification of the limits for main impurities in UF₄ [14].

Impurities	Al	В	Cd	С	Со	Cr	Cu	Fe	Mn	Ni	Si
ppm	70	0.2	0.1	150	5	25	40	75	15	40	30



Fig. 1. Uranium purification processes for fuel fabrication [11].



Fig. 2. Discharging process of uranium on a mercury drop electrode [23].

temperatures cause excessive caking on the surface of the UO_2 powder and decreases the conversion yield to UF₄. Lower temperatures increase the time required to operate. The purity level of the UF₄ powders reaches average values of 97 % [16,17].

1.2. Production of UF_4 from UO_2F_2 (wet process) [18,19]

The starting material for this process is usually UO_3 , which was dissolved in hydrochloric acid to produce UO_2Cl_2 . A suitable reducing agent reduces the UO_2Cl_2 to UCl_4 in acid medium, then UF₄ is precipitated directly by adding hydrofluoric acid. Using any reducing agent, the reaction proceeds according to the following equations:

$$UO_3 + 2HCl \rightarrow UO_2Cl_2 + H_2O \tag{3}$$

 $UO_2Cl_2 + 2R + 4HCl \rightarrow UCl_4 + 2RCl + 2H_2O \tag{4}$

 $UCl_4 + 4HF \rightarrow UF_4 + 4HCl \tag{5}$

Where R represents a reducing agent. SnCl₂ is the most common choice





Fig. 3. Uranium Pourbaix diagrams [24].

for this reaction. However, $SnCl_2$ in this process is a later neutron collector element that needs to be minimized [20]. To make up for its neutron consumption, it is necessary to increase the amount of metallic U for fuel elements manufacture.

Accordingly, the known commercial conversion processes are either complex aqueous-based operations with multiple stages or a one-stage dry process. Although wet processes are easier to control, they generate large quantities of liquid wastes. The single-step dry process produces a minimal waste stream, but is difficult to control. In addition, there is a special requirement to control the UF₄ morphology. While the UF₄ product obtained by precipitation are acicular crystals, the electrolytic process can control this parameter through current density. Spherical crystals give higher densities of UF₄ by this method. Its density ranges between $3.0-4.0 \text{ g/cm}^3$. This property gives an appreciable decrease in its size and effective volume that favors heat transfer during the subsequent operations (Fig. 1).

Fig. 2 shows the fundamentals of the dropping mercury electrode. This is an efficient method to obtain UF₄, considered as the base compound to achieve metallic uranium and other insoluble compounds in aqueous medium. The mercury electrode allows reaching negative potentials unto -2.50 V_{SCE} (Saturated Calomel Electrode), which is equivalent, in the Normal Hydrogen electrode (NHE) scale, to -2.26 V_{NHE}. Mercury is a good catalyzer to obtain a wide range of low reduction potential metallic species in aqueous solutions. It possesses high electrical conductivity and it is in liquid state at low temperatures. The constant mercury dropping flow allows the formation of mercury drops and eliminates the frequent problem of electrode passivation, which is present in solid electrodes [21]. The diameter of the mercury drops can be controlled thanks to the outlet of the decantation funnel, which defines the initial drop size, and the mercury flow that limits the grow of the drops [22]. Small diameter drops allow the application of high current densities in the cathodic reaction and the production of fine UF₄ powders.

Fig. 3 shows the uranium pourbaix diagram. In the stability range of



Fig. 4. Dropping mercury cell.

water (potentials between the lines "a" and "b"), uranium is present as UO_2^{2+} . In these conditions, reaction (6) shows the main cathodic reaction:

$$UO_2^{2+} + 4H^+ + 2e^- \to U^{4+} + 2H_2O$$
(6)

The mercury drops in contact with the aqueous medium, serve as the cathode of the cell, giving a large cathodic current density [25–27]. These drops, surrounded by the hydrofluoric acid solution and the highly electro-negative fluoride ions, allow the formation of the insoluble compound uranium tetrafluoride, eq. (7):

$$UO_{2}^{2+} + 4H^{+} + 4F^{-} + 2e^{-} \rightarrow UF_{4} + 2H_{2}O$$
(7)

The hydrogen production is a secondary reaction taking place in the mercury drop:

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \tag{8}$$

Reaction (8) took place as acid consumption in the UO_2F_2 solution. It was important to ensure a pH level of 1.0 - 1.5. According to Fig. 3, this parameter makes sure that the uranium remains dissolved as UO_2^{2+} . The main oxidation reaction was the water oxidation to oxygen:

$$H_2 O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$$
 (9)

Considering these aspects, an electrolytic process can simplify the overall production of UF₄ powders. Furthermore, this method can improve the performance of all the subsequent uranium purification stages, either to obtain uranium-based fuel plates for research reactors or uranium pellets for power reactors [28]. This study will describe this alternative procedure to obtain UF₄ using a mercury cathode-based process.

2. Experimental development

Fig. 2 shows the experimental process to obtain UF_4 using the dropping mercury electrode:

Fig. 4 shows the cell used, which utilizes the dropping mercury electrode technique. The cell was made using a 750 cm^3 separatory

funnel. A vessel with an outlet at the bottom was used to store and recirculate the mercury to the top of the funnel. The mercury flow was regulated with the drop valve. The funnel had a 3 mm outlet diameter. The grow of the mercury drops was controlled using the mercury flow and nozzles to ensure different drops sizes, from 5 to 7 mm diameter. 1500 cm³ of mercury were used for continuous operation. Mercury was recirculated using a peristaltic pump from the bottom and fed to the funnel. During the electrolysis process, the platinum anodes were separated from the cathodic area using membranes to prevent the oxygen generated from causing a partial oxidation from UF₄ to UO₂F₂. The experiments were done using a 50 g/l UO₂F₂ solution at pH values of 1.0–1.5, and temperatures between 20–65 °C. Table 2 shows the chemical analysis of the (NH₄)₂U₂O₇ uranium concentrate, with a purity level of 96 %. The chemical analyses were done using the ICP-mass spectrometry.

To decrease the evaporation rate, the surface of the solution was covered with polystyrene balls, which did not show weight loss or deformation with heat in any test. Although the vapor pressure of mercury is low (0.002 mm Hg) at 24 °C, an atmosphere fully saturated with mercury vapor contains approximately 18 mg/m³, which can be dangerous to health. As a containment measure for mercury evaporation, the cell was sealed inside an acrylic box and a sulphide carbon trap for mercury adsorption. This prevented any kind of mercury leaking from the cell.

All the experiments were carried out using a GW instek GPR-6030D Linear DC power cell, in galvanostatic mode, inside a stainless steel reactor, coated inside with Teflon or PVC, resistant to HF corrosion. Fig. 4 shows that the mercury in the glass funnel was polarized through the contact of an iron electrode and the anodes were circular platinum sheets of 0.2 mm thick and 30 mm in diameter.

Another important aspect of the system to consider is the stability in time. The dropping mercury electrode allows regulating the size of UF₄ particles through the mercury flow. However, the dropping Hg cell needed careful control of Hg flow and possible Hg oxidation. This was necessary to maintain the electrical current through the electrochemical cell. The liquid mercury, once it gets separated from iron connection, the electric connection is interrupted and it can be oxidized in the presence of oxygen, according to Eq. (10) [30].

$$Hg_{(l)} + \frac{1}{2}O_2 \rightarrow HgO_{(s)} \tag{10}$$

This reaction can take place with the oxygen generated by the anode. However, the membranes separating the anode from the mercury prevented the mercury oxidation.

Fig. 2 illustrates the electrochemical process taking place when a mercury drop gets in contact with the UO_2F_2 solution. When the mercury drops losses the electrical contact with the iron cathode, the UF₄ deposit stops its growth. This mechanism prevents the accumulation of solid products on the cathodic surface. Because of this, the current intensity cannot increase indefinitely when the electromotive force increases. Instead, the current intensity reaches a constant limiting value, for determined ionic species. The maximum cathodic current density is directly proportional to the concentration of the electro-reducible substrates, which can be UO_2^{2+} , or protons (H⁺) from the free acid, when the current intensity surpasses its maximum value for uranium transport. For these reasons, the main variables to control the UF₄ production are the continuous mercury flow, to keep the mercury drop diameter constant, pH to ensure that uranium was dissolved, and the current intensity [29].

The UF₄ samples were deposited along with the Hg, which was

Table 2

Chemical analysis of the main impurities of the ammonium diuranate.

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Impurities	Al	В	Cd	С	Со	Cr	Cu	Fe	Mn	Ni	Si
ppm	1500	30	40	400	500	300	200	1200	300	600	150



Fig. 5. Current efficiency v/s current intensity, for a mercury drop of 5 mm.



Fig. 6. Cathodic current densities v/s current intensity, for different mercury drop sizes.

drained with a peristaltic pump after every 24 h. UF₄ was extracted, filtered, and washed with hot deionized water. Subsequently, it was dried at 70–80 $^{\circ}$ C in an air-nitrogen atmosphere. The products obtained was characterized through XRD and chemical analysis of impurities using ICP-mass Spectrometry.

3. Results and discussions

Fig. 5 shows the influence of the current intensity and temperature over the current efficiency of the process.

Fig. 5 shows that both temperature and current intensity have important consequences over the current efficiency. Although the temperature improves the current efficiency in all cases because of the reduction in the ohmic resistance of both Hg and the HF solution, it is not safe to increase it over 65-70 °C. The system can work at higher

temperatures, but it is not recommendable due to the effect of HF evaporation. The reason for the loss of current efficiency for current intensities above 1.57 A was the protons reduction to hydrogen, reaction (8). This was verified in the final pH value of the UO_2^{2+} solution, which were from 2.5 to 4.0. To avoid possible uranium precipitation because of the acid consumption, HF acid and UO_2F_2 were replenished after every 24 h test.

Fig. 6 illustrates the effect of the mercury drop size obtained through the mercury flow. This drop size allows reaching cathodic current density values up to 80.000 A/m². This was the reason of the UF₄ particle size. The current density in the cathode must be large to obtain fine UF₄ powders. However, in accordance to Fig. 5, a current density of 20.000 A/m² (1.57 A – 5 mm drop diameter and 65 °C) was the maximum value allowed before the system undergoes high current efficiency losses.

Figs. 7 and 8 show the XRD of a UF₄ sample. The X-ray diffraction analysis shows that the product obtained was anhydrous UF₄. The inert gas removed the humidity present. The density of the UF₄ sample was measured using picnometry. The values reached were between $3.0-3.5 \text{ g/cm}^3$, achieving good compaction of the UF₄ powders. This allows better heat transfer during the following uranium tetrafluoride reduction using Mg and the rest of the nuclear fuel cycle stages. Table 3 shows the chemical composition of the UF₄ sample.

Fig. 9 shows the morphology of the UF₄ sample obtained using a current intensity of 1.57 A and mercury drop size of 5 mm. It was found that the shape of the particles was essentially spherical. Fig. 10 shows a UF₄ sample obtained by conventional chemical reduction, using SnCl₂ [28]. The UF₄ product obtained with the dropping mercury electrode stopped its growth at the moment the mercury drop separates itself from the electrical connection provided by the iron cathode, yielding fine



Fig. 8. X-ray diffraction Zoom, showing the characteristic UF₄ peaks.



Fig. 7. X-ray diffraction, showing the full spectra analyzed.

Table 3

Chemical analysis of the main impurities in UF₄ powders.

Impurities	Al	В	Cd	С	Со	Cr	Cu	Fe	Mn	Ni	Si	UF ₄
ppm	25	20	10	0.5	15	20	15	50	25	30	5	>98 %



Fig. 9. SEM image of a UF₄ sample at (left) 200X and (right) 800X.



Fig. 10. UF₄ sample obtained from the wet process using $SnCl_2$ as reducing agent [30].

powders. Meanwhile, the conventional chemical reduction process gives UF_4 powders with irregular morphologies because of the continuous growth mechanisms during the chemical reduction reaction.

4. Conclusions

The main conclusions for this work were the followings:

- The traditional methods to obtain UF4 fulfill their purpose of supplying this material for the nuclear fuel cycle. Nevertheless, they are very complex and do not allow appropriate control over grain size, density and morphology. The properties of the mercury as a liquid electrode gave the opportunity to develop an electrolytic process to control the UF4 production through UO2F2 concentration, temperature, current density and mercury flow.
- The proposed electrochemical process allowed obtaining UF4 powders with properties and purity levels, according to the requirements for its direct use in the nuclear fuel cycle. The safety execution of this method was possible thanks to the correct use of the stainless steel reactor, to avoid corrosion by HF. Iron was an adequate connector, since it does not form amalgams with mercury. The adequate security measures, such as hermetically closed reactors and mercury traps, allow the application of this process at an industrial level and, in turn, a high-quality product to be obtained in a single step.

- The stability of the operation depended on the following conditions: the uranium and acid concentrations in the aqueous phase, the continuous mercury flow through the cell to avoid interruptions in the UF4 production, and the isolation of the anode from the rest of the system, to avoid the oxidation of the UF4 to UO2F2 and the Hg oxidation to HgO. Replenishing the initial UO2F2 and the acid concentrations after every test allowed the system to keep a constant current efficiency through time. The membrane used to separate the anode from the rest of the system prevented the oxidation problems.
- An important aspect of this process is the effect of the current intensity and the temperature over the global efficiency. Increasing the temperature of the UO2F2 solution allows achieving higher efficiencies, but this result is limited by the evaporation of the solutions. While high current intensities increase the UF4 production, they also decrease the efficiency. For the proposed system, any condition of current densities below 20.000 A/m2 (this was 1.57 A, mercury drop of 5 mm and temperature of 65 °C), kept the overall system working with current efficiencies over 90 %. All the tests were done using 50 g/L UO2F2 solutions. Using higher UO2F2 concentrations (the electro-reducible species) would increase the overall efficiency and allow higher current densities.
- The proposed electrolytic process allowed controlling the UF4 particle size for the metallothermic process. The current UF4 precipitation by SnCl2 do not allow particle size control, and it forces to do an additional milling stage of the UF4 powders. This process yields UF4 directly to the metallothermic reduction with Mg, which can be beneficial to the uranium industry.
- The diameter of the Hg drop has a great influence on the cathodic current density. Smaller diameter drops raise the current density, and the lack of growth of the UF4 product allows obtaining fine UF4 powders.

Declaration of Competing Interest

None.

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