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ALTERNATIVE PROCESS TO PRODUCE UF_4 USING THE EFFLUENT FROM AMMONIUM URANYL CARBONATE ROUTE

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ABSTRACT

The Nuclear Fuel Centre of IPEN / CNEN - SP develops and manufactures dispersion fuel with high uranium concentration. It meets the demand of the IEA-R1 reactor and future research reactors to be constructed in Brazil. The fuel uses uranium silicide (U_3Si_2) dispersed in aluminum. For producing the fuel, the process of uranium hexafluoride (UF_6) conversion consist in obtaining U_3Si_2 and / or U_3O_8 through the preparation of intermediate compounds, among them ammonium uranyl carbonate - AUC, ammonium diuranate - DUA and uranium tetrafluoride - UF_4. This work describes a procedure for preparing uranium tetrafluoride via a dry route, using as raw material the filtrate generated when ammonium uranyl carbonate is routinely produced. The filtrate consists mainly of a solution containing high concentrations of ammonium (NH^{4+}), fluoride (F^{-}), carbonate (CO^{3-}) and low concentrations of uranium. The procedure consists in recovering NH_4F and uranium, as UF_4, through the crystallization of ammonium bifluoride (NH_4HF_2) and, in a later step, the addition of UO_2, occurring fluoridation and decomposition. The UF_4 obtained is further diluted in the UF_4 produced routinely at IPEN / CNEN-SP by a wet route process.

1. INTRODUCTION

At Institute of Energy and Nuclear Research (Instituto de Pesquisas Energéticas e Nucleares ï IPEN/CNEN-SP), radioisotopes, radiopharmaceuticals and other nuclear medical substances are produced, processed and distributed. Considering the social and strategic importance of the radiopharmaceutical production in Brazil, it was decided to raise de power of the IEA-R1 reator from 2 to 5MW, and extend the operation time to 100 continuous hours weekly. This will provide conditions to produce the Molibdenum-99, which is the raw material of tecnecium-99m. Due to these circunstances, the expansion of fuel elements capacity of production, with a new unit of production in Nuclear Fuel Centre (Centro de Combustível Nuclear ï CCN), is mandatory. In this sense, higher yields processes have always been under development.

At CCN, a centre located inside the IPEN/CNEN-SP, the adopted processes of UF_6 reconversion for nuclear elements production consist in obtaining U_3O_8 and/or U_3Si_2 [1] from intermediate compounds, among them, ammonium uranyl tricarbonate (ACU), ammonium

diuranate (ADU) and uranium tetrafluoride (UF_4). In all of these routes liquid effluents are generated, which have compositions that forbid it release to environment. However, with proper chemical treatment, some effluents could be reused in the procedure, reducing the amount of total effluents and providing a more efficient and reasonable process.

This work proposes an alternative chemical process [2] that aims to obtain UF_4 using as raw material a fluoride effluent generated UF_6 conversion process, specifically, from the ammoniumperoxidefluorouranate (APOFU) step [3].

2. MATERIALS AND METHODS

2.1.Raw material

The fluorinated effluent, generated at the recoversion processes of UF_6 to ACU, is based in the following reaction:

$$UF_{6\,(g)} + 5H_2O_{\,(l)} + 10\,NH_{3\,(g)} + 3CO_{2\,(g)} \rightarrow (NH_4)_4UO_2(CO_3)_{3\,(s)} + 6NH_4F(aq) \qquad (1)$$

At ACU generation unit, the produced effluent consists in a solution of ammonium fluoride (NH_4F) with high concentration of CO^{3-}, NH^{4+}, F^-. The uranium concentration lies around 300 mg L^{-1}. This is treated with hydrogen peroxide, resulting in the APOFU [3]. The effluent of this last step still contains significant concentration of uranium, ammonia and fluoride, and represents the raw material of this work.

2.2. Crystallization of ammonium bifluoride

The solution was concentrated by heating at 95°C. It allowed reduction of the solution to about 25% of its initial volume, and crystallization of NH_4HF_2 (ammonium bifluoride) when cooled.

2.3. Fluoridation of uranium dioxide

Experiments were carried out using as starting materials NH_4HF_2 and uranium dioxide (UO_2) [4, 5 e 6]. The temperature was fixed at 150°C, slightly higher than the melting temperature of NH_4HF_2 (124.6°C) [7]. This temperature is sufficient for the reaction to occur, and the water formed is easily released, avoiding the formation of UO_2F_2. The duration of the experiments was varied between 2 and 24 hours. The process is based on the following reaction:

$$12UO_2 + 31NH_4HF_2 \rightarrow 2(NH_4)7U_6F_{31} + 17NH_3 + 24H_2O \quad (2)$$

2.4. Decomposition to uranium tetrafluoride

The influence of temperature (400 and 500°C) and time (between 2 and 36 hours), were studied, at inert atmosphere of argon (analytical grade, 5.0). The process takes place according to the following reaction:

$$(NH_4)_7U_6F_{31(s)} \rightarrow 6UF_{4(s)} + NH_4F_{(g)} \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Chemical characterization of effluent

The effluent initially used in this work was characterized chemically and the results are presented at Table 1.

Table 1 - Composition of the used filtrate

Ion	Average concentration
U^{+6}	2.03 mg.L^{-1}
NH_4^+	80.1 g.L^{-1}
F^-	110 g.L^{-1}
$CO_3^{--} + HCO_3^-$	0.34 g.L^{-1}

These results confirmed the high concentration of ammonia and fluorides. In addition, the concentration of uranium exceeded the maximum permitted by CONAMA [8] for disposal.

3.2 Crystallization of NH_4HF_2

The NH_4HF_2 obtained was characterized by X-ray diffraction (Figure 1). The diffraction peaks of the compound NH_4HF_2 were confirmed by the JCPDS 12-0302 card catalog of the *Powder Diffraction File* [9], and, despite the presence of a small amount of ammonium fluoride (NH_4F), this fluoridation route seems as efficient as the bifluoride process.

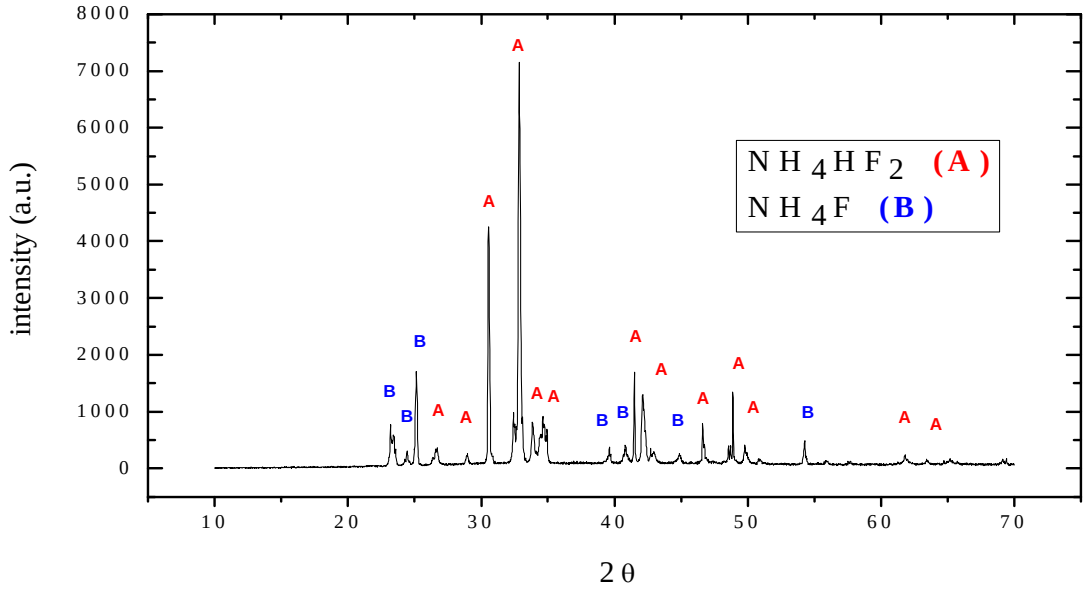


Figure 1 - X-ray diffraction patterns of NH_4HF_2 obtained from the processing of the filtrate

3.3 Fluoridation

After fluoridation experiments, samples were submitted to X-ray diffraction analysis. The compound obtained after fluoridation was characterized as $(NH_4)_7U_6F_{31}$, equivalent to the 16-756 JCPDS card catalog of the *Powder Diffraction File* [9]. The X-ray diffractogram is shown in Figure 2.

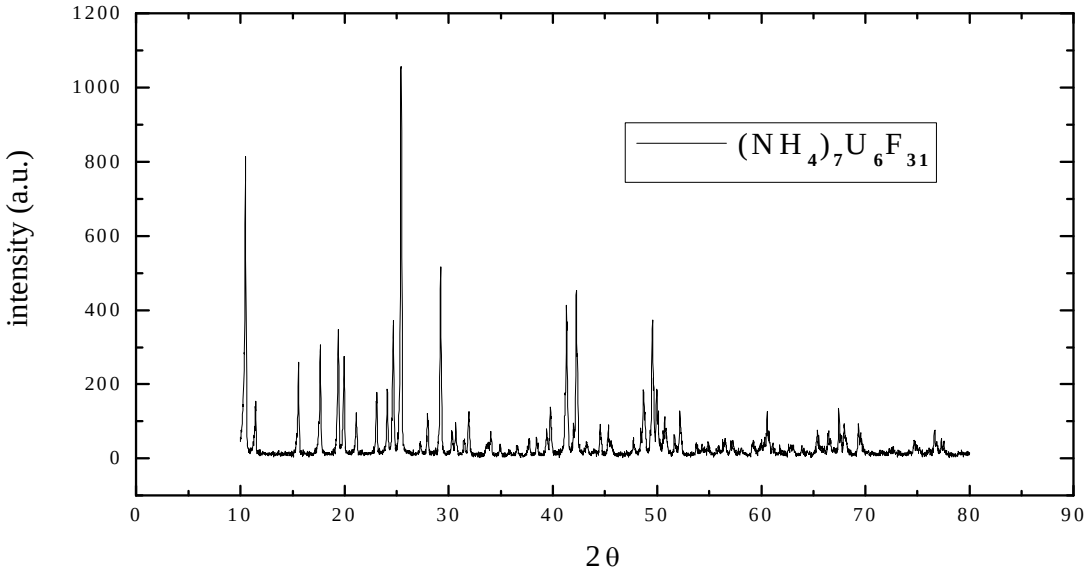


Figure 2 - X-ray diffraction patterns of samples obtained after fluoridation.

3.4 Decomposition

Tests were carried out to verify the shortest time necessary for the fluoridation of UO_2. The results are shown in Figure 3:

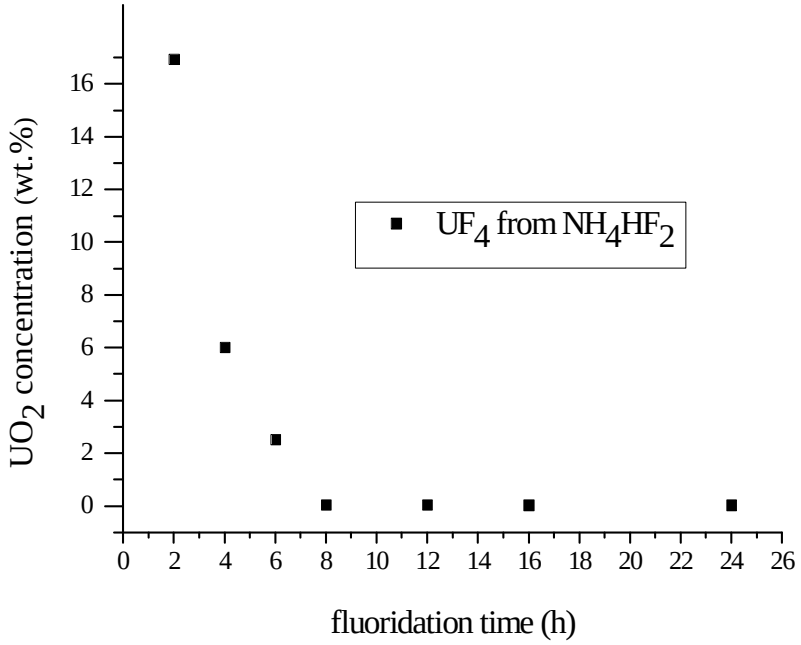


Figure 3 - Influence of time in fluoridation of UO_2.

It can be seen in the graph shown in Figure 3 that the minimum time required for a reaction with satisfactory fluorination is 8 hours. Shorter times result in a UF_4 with high concentration of unconverted uranium oxides, which are insoluble in aqueous solution of ammonium oxalate. Longer times are unnecessary, due the fact that after 8 hours the fluoridation reaction yield remains stable, with an average concentration of 0.04% UO_2 in UF_4.

To confirm the minimum temperature required for a complete decomposition of $(NH_4)_7U_6F_{31}$ to UF_4, additional studies of differential thermal analysis with simultaneous thermogravimetric analysis were performed on samples of $(NH_4)_7U_6F_{31}$ and UF_4. The results can be seen in Figure 4.

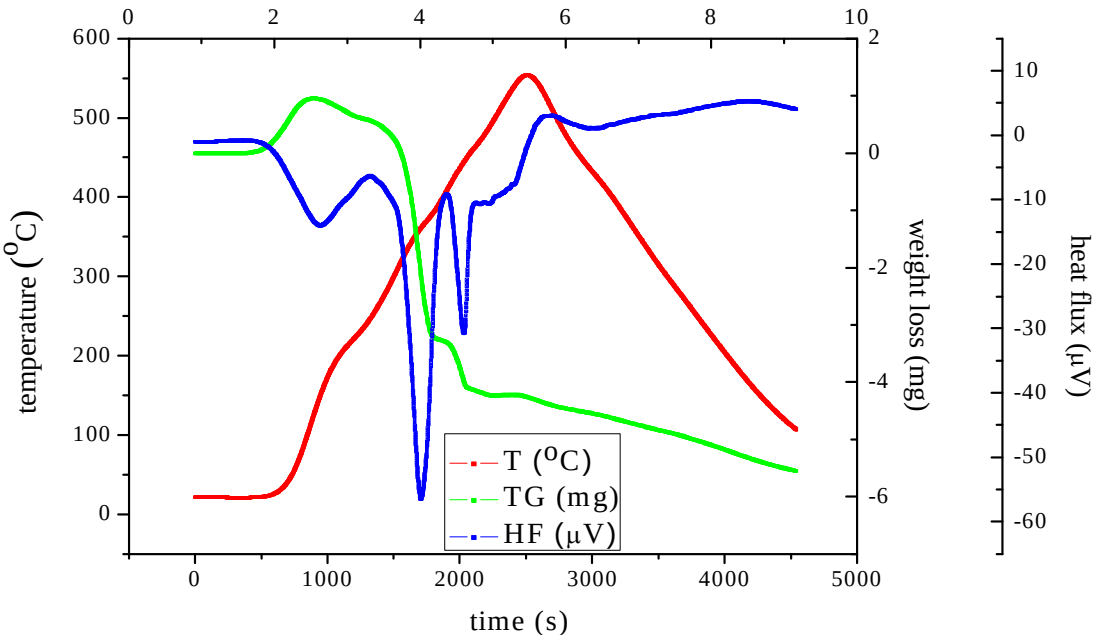


Figure 4 - Thermogravimetry and differential thermal analysis of $(NH_4)_7U_6F_{31}$ samples

It was analyzed the mass loss of the sample over the period of testing. From an initial mass of 40.9 mg, final mass loss was equal to 5.545 mg, corresponding to 13.5wt.%, close to the theoretical value is 12.1wt.% This result indicates that the mass release by the reaction of decomposition of $(NH_4)U_6F_{31}$ was adequate, leading to the formation of UF_4.

The curve of heat flow versus time shows the decomposition of $(NH_4)UF_5$. Up to 350C°, the primary mass loss is due to the ammonia release of the system. Subsequently, up to 500°C, there is secondary release of NH_4F. In this work, the primary release event started at 306°C with a maximum at 360°C, and the secondary release began at 407.4°C, with a maximum at 464.4°C. These results are comparable to literature [6].

3.5 Product Characterization

Physical and chemical properties of the UF_4 obtained via NH_4HF_2, and UF_4 routinely produced at IPEN-CNEN/SP via $SnCl_4$ [10], are presented in Table 2.

Table 2 ï Physical and chemical characteristics of UF_4

	UF_4 via $SnCl_2$	**Obtained UF_4**
UF_4 (wt.%)	99.85	98.69
UO_2F_2 (wt.%)	0.34	1.27
UO_2 (wt.%)	0.29	0.04
Poured density (g/cm^3)	2.12	0.86
Tapped density (g/cm^3)	2.65	1.19
Specific surface area (m^2/g)	0.21	2.85

The reduction process that is routinely done at IPEN/CNEN-SP tolerates up to 4wt.% of UO_2 + UO_2F_2 impuritires. In this sense, the UF_4 obtained meets the specifications. Additionally, the density of the UF_4 obtained in this study is relatively low. However, it should not be a problem, because it will be diluted in UF_4 batches routinely produced at IPEN/CNEN-SP. Moreover, it appears that the UF_4 obtained presents a specific surface area more than ten times greater than the ordinary produced UF_4, which indicates a more reactive powder.

For comparison purposes, the Figure 5 shows two X-ray diffractograms, of the UF_4 obtained via aqueous, using tin chloride as reducing agent, and the UF_4 produced in this work. The diffracted patterns can be confirmed by letter 32-1401 of the JCPDS *Powder Diffraction File* catalog [9].

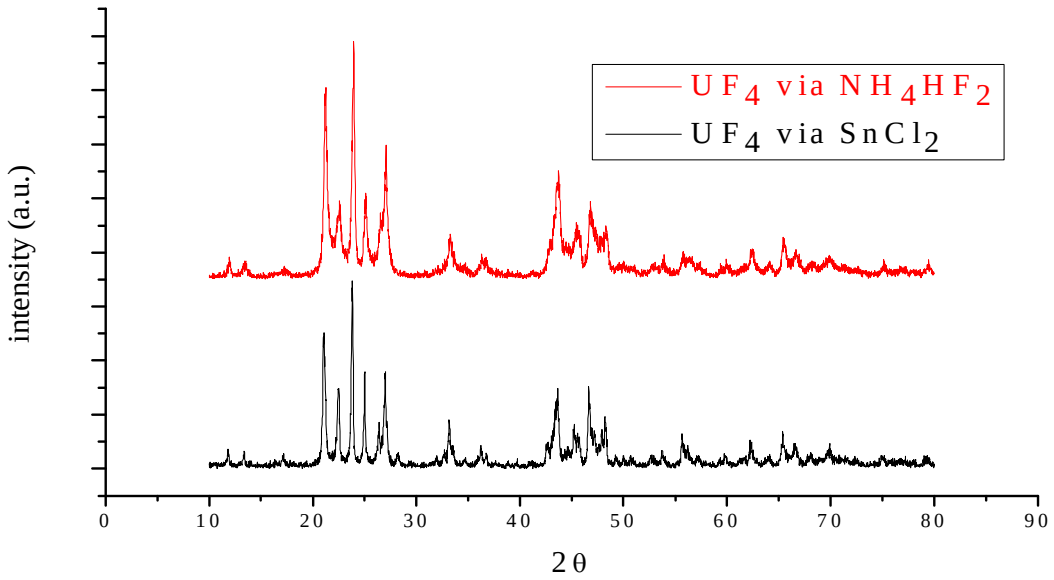


Figure 5 ï X-ray diffractograms of UF_4 produced by different routes

4. CONCLUSIONS

The presented process can be represented in figure 6. The UF_4 mass produced (1726,7g) indicates a yield close to theoretical values, which would be about 1731g, in the case of starting with 1488,5 g de UO_2. The best conditions for obtaining UF_4 via ammonium bifluoride recommended in this work are: fluoridation temperature of 150°C for 8 hours and decomposition temperature 500°C for 2 hours.

The obtained UF_4 has adequate chemical and physical characteristics for its utilization as raw material for metallic uranium production. Even though its low apparent density, this should not interfere at posterior processes.

The development of this process offers an efficient way to recover uranium and ammonium fluoride, reducing the amount of effluent generated, and optimizes the U_3Si_2 / U_3O_8 production yield at IPEN-CNEN-/SP.

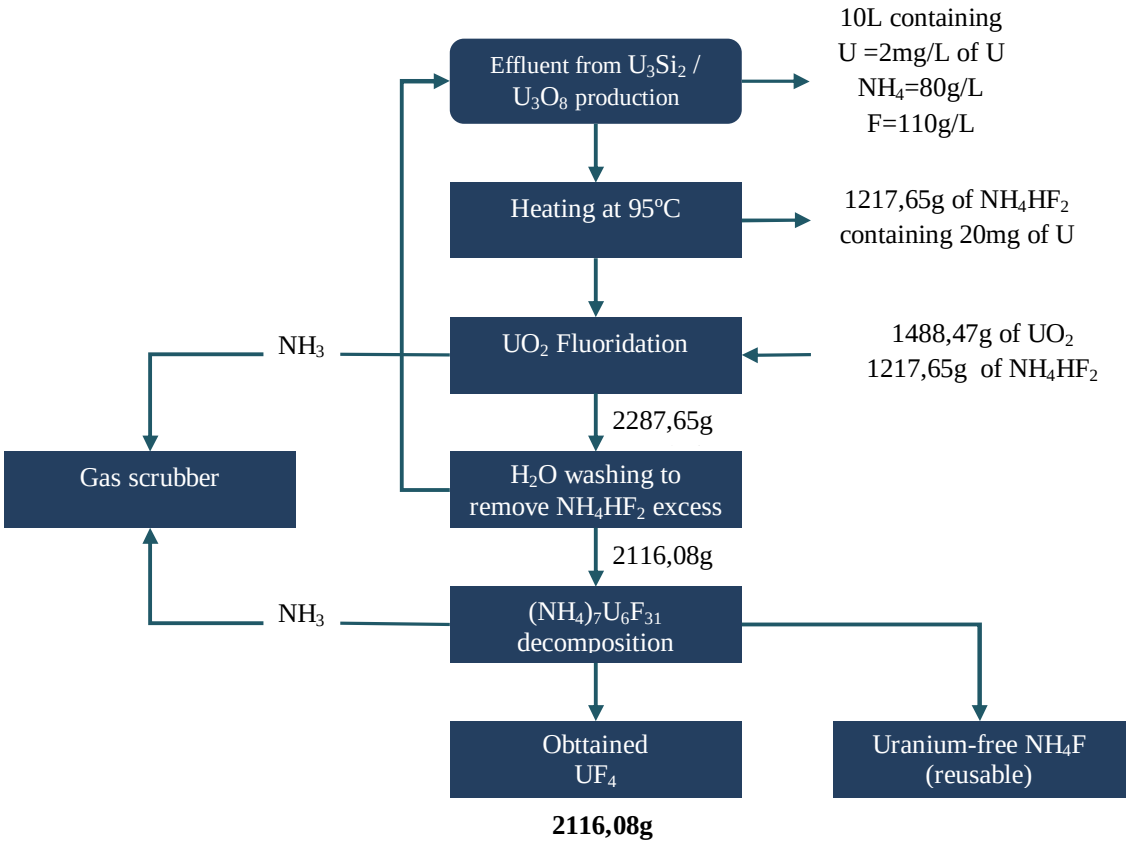


Figure 6 - Proposed process for obtaining UF_4 from effluent

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