

Dry uranium tetrafluoride process preparation using the uranium hexafluoride reconversion process effluents.

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ABSTRACT

It is a well known fact that the use of uranium tetrafluoride allows flexibility in the production of uranium silicide and uranium oxide fuel. To its obtention there are two conventional routes, the one which reduces uranium from the UF₆ hydrolysis solution with stannous chloride, and the hydrofluorination of a solid uranium dioxide. In this work we are introducing a third and a dry way route, mainly utilized to the recovery of uranium from the liquid effluents generated in the uranium hexafluoride reconversion process, at IPEN/CNEN-SP. Working in the liquid phase, this route comprises the recuperation of ammonium fluoride by NH₄HF₂ precipitation. Working with the solid residues, the crystallized bifluoride is added to the solid UO₂, which comes from the U miniplates recovery, also to its conversion in a solid state reaction, to obtain UF₄. That returns to the process of metallic uranium production unit to the U₃Si₂ obtention. This fuel is considered in IPEN-CNEN/SP as the high density fuel phase for IEA-R1m reactor, which will replace the former low density U₃O₈-Al fuel.

1. INTRODUCTION

In the Nuclear and Energy Research Institute – IPEN-CNEN/SP, radioisotopes, marked substances, radiopharmaceuticals and other materials, all of them used in nuclear medicine, are being regularly produced, processed, and distributed. They are responsible for the supply of the demand of 360 clinics, hospitals and universities in Brazil, allowing the assistance of 1,000,000 patients per year, a number which is growing at a rate higher than 20% a year.

If we consider the social and strategical importance of the radiopharmaceuticals production in our country, and the continuous demands in the radioisotopes importation needed to supply this production, our Federal Government, by its Strategic Issues Secretariat and the Nuclear Energy National Commission, recently decided, to invest in an incisive way, mainly in the IPEN/CNEN-SP, its main institute working in this field. The decision of the IEA-R1 reactor power enhancement from 2 to 5 MW and to the change of the operation schedule to 100 hours / week continuously, created the conditions to the production of an important radioisotope, molybdenum-99, of a great social impact, from the technetium-99 obtention. Works like this are being developed in cooperation with the International Atomic Energy Agency and the China Power Institute.

The growth of the IEA-R1 power from 2 to 5 MW and also of its operational regime, led to the need of the enhancement of the actual capacity in the fuel elements production, due to the enhancement in the reactor fuel consumption under these new operational conditions. For a long time, IPEN/CNEN-SP worked in the development of the fabrication processes of the nuclear fuel elements, aiming to its independence on both the production and on its capabilities of technological development.

Since its birth and during almost three decades, in a time of uncertainties relating to the nuclear materials international market, IEA-R1 reactor was totally dependent of the nuclear fuel elements importation needed to its operation, supplied during this time by the american GENERAL ATOMICS (93% in ^{235}U) and NUKEM (20% in ^{235}U), from Germany.

This context determined the creation of a new production facility at the IPEN Nuclear Fuel Center, planned to use U_3O_8 powder and U_3Si_2 ^{1/} as a dispersed fuel phase in the fuel elements, which allowed good flexibility in its U_3O_8 and U_3Si_2 fuels production capabilities. Figure 1 presents a block-diagram of the UF_6 reconversion processes, to the obtention of UF_4 (U_3Si_2) and U_3O_8 , raw-materials to the IPEN nuclear fuels.

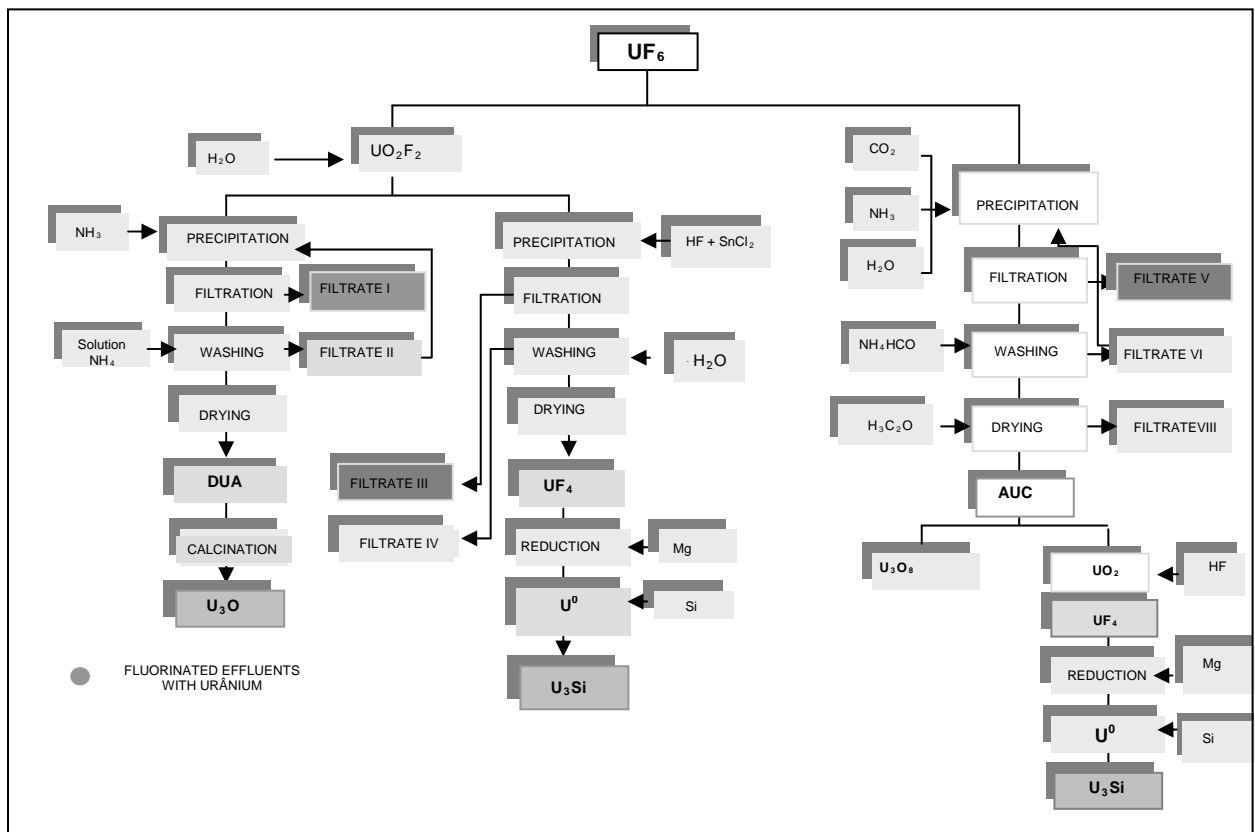


Figure 1. Block-diagram of the reconversion processes of UF_6 , to the obtention of U_3Si_2 and U_3O_8 , via DUA, UF_4 and AUC.

In the Nuclear and Energy Research Institute, IPEN/CNEN-SP, the UF_6 reconversion processes adopted to the production of nuclear fuel elements comprises the U_3O_8 and/or U_3Si_2 obtention by means of intermediate compounds preparation routes, among them the ammonium and uranium tricarbonate - AUC, ammonium diuranate - DUA and uranium tetrafluoride - UF_4 .

The objective of this work is to develop an alternative chemical process to the obtention of uranium tetrafluoride (UF₄), using as raw-material a form of fluorinated effluent, generated in the UF₆ reconversion process, used in the production of nuclear fuel elements. More specifically, in this work, we are dealing with the originated in the AUC obtention.

The production of metallic compounds of uranium passes to the obtention of metallic uranium itself, which was firstly produced, from UF₄^{/2/}, in 1894. Today, all the world metallic uranium production comprises the magnesiothermic or calciothermic reduction of UF₄^{/3/}.

Uranium tetrafluoride obtention can be achieved by several processes, divided in two classes, the dry and the wet ones^{/4-8/}.

2. EXPERIMENTAL PROCEDURE

AUC obtention is based in the following reaction:



In the AUC obtention unity are mainly produced two effluents: the filtrate V, form the first filtration of AUC, and the filtrate VI, formed basically by ethanol (H₅C₂OH) used in the AUC washing, aiming the humidity reduction.

2.1. Raw-Materials

We called as filtrate V the raw-material used in this work, formed mainly by an ammonium fluoride solution (NH₄F) with high CO₃⁼, NH₄⁺, F⁻ concentration and traces of uranium. In table 1 are showed the main chemical and physical characteristics of filtrate V.

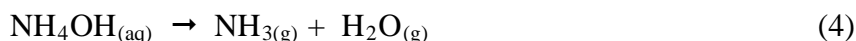
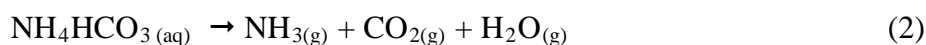
Table 1. Physical and chemical properties of filtrate V.

Ion	Mean concentration	Metallic Impurities	µg/g
U(VI)	300mg.L ⁻¹		
CO ₃ ⁼ + HCO ₃ ⁻	80g. L ⁻¹	Cd,Al,Mg,Mn	<2
NH ₄ ⁺	110g. L ⁻¹	Ca,B,Zn,Mo	2,6
F ⁻	100g. L ⁻¹	Ni,Cu,Cr	10
		Fe	10,5
Density	1.080g.cm ⁻³		
pH	9.0		

In this process there are two main steps. The first one is the uranium precipitation as uranium peroxide^{/9/} and the next is the dry-way uranium precipitation as uranium tetrafluoride

2.2. Uranium Precipitation as Uranium Peroxide

Filtrate V from the conversion of UF₆ to AUC was transferred to the decarbonating reactor with flow of air and mechanical stirring at 95⁰C for 30 minutes, to ensure the optimal conditions to the uranium precipitation, according to the following equations:



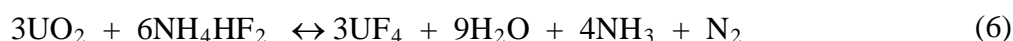
The filtrate, now poor in carbonate ions, was transferred to the precipitation reactor together with flow of air and ammonium, added until pH 8,5, under the temperature of 60⁰C. Slowly and constantly, H₂O₂ 30% was added with mechanical stirring to the system. From this technique an uranium compound, called ammonium-peroxidefluoruranate –APOFU, could be produced. The reaction is:



2.3. Dry-Way Uranium Precipitation as Uranium Tetrafluoride

The solution was left at rest for 15 hours and its upper part, almost 90% in volume, was sent to the concentrator. It consisted of a NH₄F solution with uranium concentration between 6-7mg.L⁻¹. The uranium content in this solution does not allow its discharge to the environment.

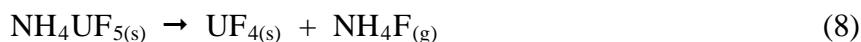
UF₄ can be prepared by the ammonium fluoride or bifluoride reaction with UO₂ according to the following equation^{/10-12/}:



The fluorinated solution (NH₄F) passed to a concentration process under the temperature of 95⁰C. When the volume reduction was about 75% of its initial volume, and after some cooling, NH₄HF₂ crystallises. This product was washed with ethanol, to the remotion of moisture. The NH₄HF₂ obtained was added to UO₂ with an excess of 20% relative to the stoichiometric calculated, and then transferred to a fluorination reactor, made with Teflon. The fluorination reaction was carried out for 12 hours at 150⁰C, according to:



and the decomposition was carried out at 400⁰C for a period of 2 hours under analytic argon 5.0 atmosphere, according to the following equation:



3. RESULTS AND CONCLUSIONS

The obtained UF₄ was chemically and physically characterized, by XRay-diffraction, scanning electron microscopy (SEM), determination of its specific surface area by the BET method, the mean particle diameter by the CILAS method and specific mass by Helium

picnometry. Its chemical and physical properties were presented in table 2, compared with the stannous chloride route, traditionally used at IPEN/CNEN-SP.

Table 2 – Mean values of the chemical and physical properties.

	UF ₄ via SnCl ₂ ^{13/}	UF ₄ via NH ₄ HF ₂
UF ₄ (%)	99,85	98,69
UO ₂ F ₂ (%)	0,34	1,27
UO ₂ (%)	0,29	0,04
Apparent density (g cm ⁻³)	2,12	0,86
Tap density (g cm ⁻³)	2,65	1,19
Specific mass (g cm ⁻³)	6,70	6,60
Mean particle diameter (µm)	15,00	4,56
Specific surface area (m ² g ⁻¹)	0,21	2,85

In figure 2 are presented the spectra of both UF₄ produced by the method presented in this work and from the aqueous route, used in the production of the fuel elements in IPEN-CNEN/SP. In figure 3 are presented a typical SEM image of the obtained UF₄. It indicates a granular and porous powder structure, as represented bellow.

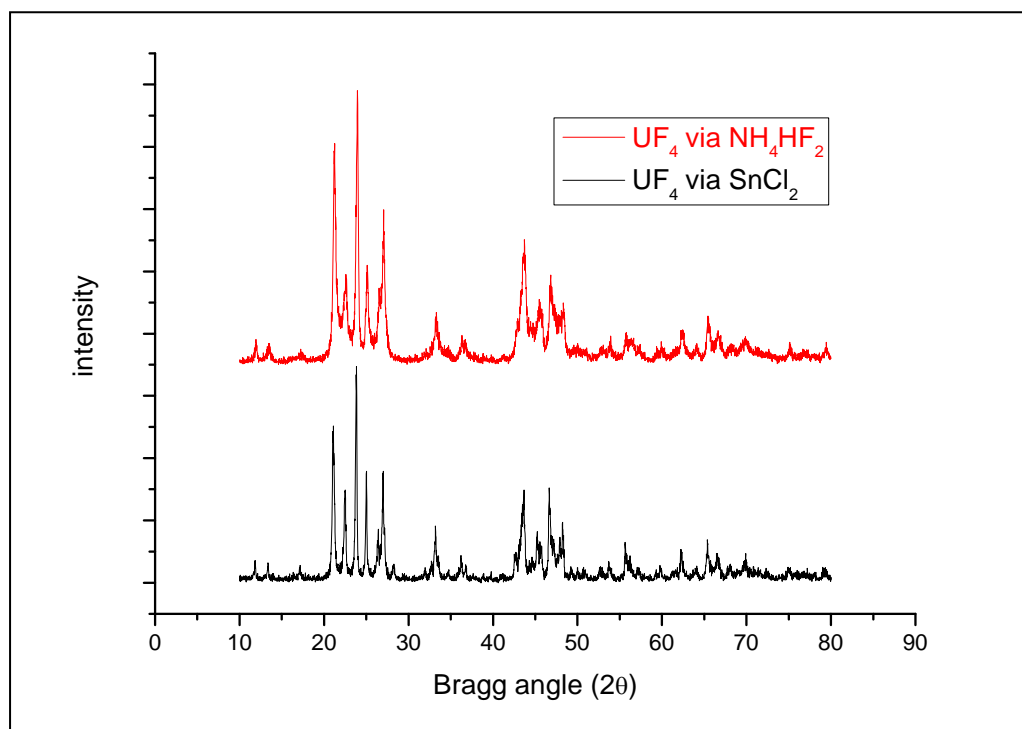


Figure 2 – XRay-diffraction pattern of UF₄ produced by the bifluoride route and from the aqueous route .

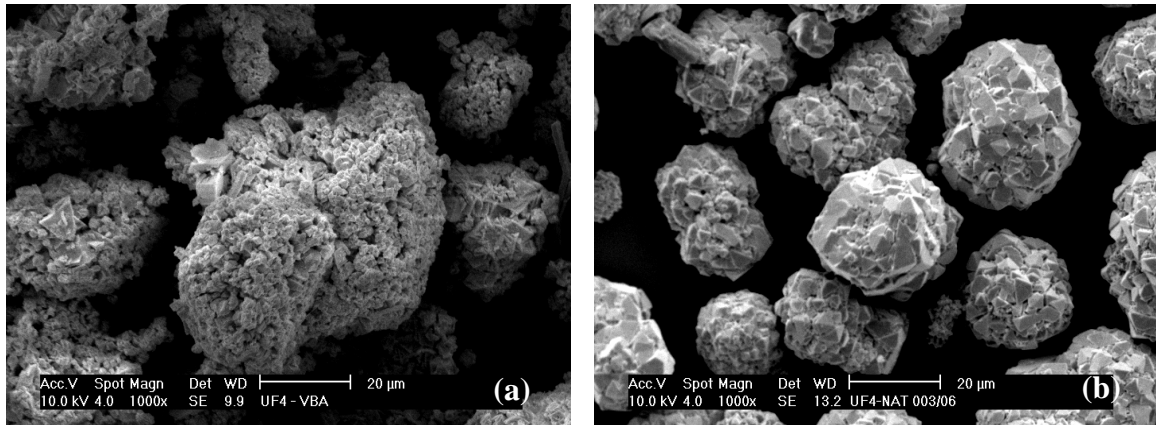


Figure 3 – SEM image of some UF₄ particles, bifluoride(a) route and via SnCl₂ (b).

This work showed that it is perfectly possible to prepare UF₄ using ammonium bifluoride as the fluorination media, from the effluent generated in the UF₆ conversion to AUC. The UF₄ obtained has the same crystalline structure presented by the aqueous process here utilized in IPEN-CNEN/SP, as demonstrated by the X-Ray spectrum. Besides, it has the correct chemical and physical characteristics for its usage in the metallic uranium obtention. Even presenting a lower relative tap density, this property will not be a problem, because this is an alternative process that has as main goals the recovery of uranium, ammonium and the fluorides of the liquid effluents generated in the process of UF₆ reconversion, and this UF₄ will be later diluted in the UF₄ charges produced in IPEN - CNEN/SP by the aqueous route.

A new set of tests of UF₄ incorporation in the UF₄ used in the production of fuel elements routines are scheduled, as a way to verify the behaviour of this new product.

The development of this new process offers an improvement in the uranium recovery processes of secondary sources, by a route which eliminates environmental pollution. Also, it offers a new chemical compound with physical and chemical characteristics very similar to that usually produced at IPEN/CNEN-SP.

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