



Original Article

Production of uranium tetrafluoride from the effluent generated in the reconversion via ammonium uranyl carbonate



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ABSTRACT

Uranium tetrafluoride (UF₄) is the most used nuclear material for producing metallic uranium by reduction with Ca or Mg. Metallic uranium is a raw material for the manufacture of uranium silicide, U₃Si₂, which is the most suitable uranium compound for use as nuclear fuel for research reactors. By contrast, ammonium uranyl carbonate is a traditional uranium compound used for manufacturing uranium dioxide UO₂ fuel for nuclear power reactors or U₃O₈-Al dispersion fuel for nuclear research reactors. This work describes a procedure for recovering uranium and ammonium fluoride (NH₄F) from a liquid residue generated during the production routine of ammonium uranyl carbonate, ending with UF₄ as a final product. The residue, consisting of a solution containing high concentrations of ammonium (NH₄⁺), fluoride (F⁻), and carbonate (CO₃²⁻), has significant concentrations of uranium as UO₂²⁺. From this residue, the proposed procedure consists of precipitating ammonium peroxide fluorouranate (APOFU) and NH₄F, while recovering the major part of uranium. Further, the remaining solution is concentrated by heating, and ammonium bifluoride (NH₄HF₂) is precipitated. As a final step, NH₄HF₂ is added to UO₂, inducing fluoridation and decomposition, resulting in UF₄ with adequate properties for metallic uranium manufacture.

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1. Introduction

The Nuclear and Energy Research Institute (IPEN/CNEN-SP) produces and distributes radioisotopes, radiopharmaceuticals, and other nuclear medical substances. Considering the social and strategic importance of radiopharmaceutical production in Brazil, it was decided to raise the power of the IEA-R1 reactor from 2 MW to 5 MW, and extend the operation time to 100 continuous hours weekly. This provided conditions to increase radioisotope production. Due to these circumstances, expansion of the capacity for fuel element production was mandatory. In this sense, processes aiming at higher yields have always been under development.

The processes adopted for UF₆ reconversion to produce nuclear fuel consist of obtaining uranium compounds from various intermediate compounds, among them ammonium uranyl tricarbonate

(AUC), ammonium diuranate, and uranium tetrafluoride (UF₄). All of these routes for the production of these compounds generate liquid effluents with compositions that are restricted for environmental disposal. To reduce the amount of total effluent generated and improve the efficiency of the process, it is highly desirable to develop proper chemical treatments that allow the reuse of some effluents in the process.

UF₄ is an important uranium compound for the nuclear industry. Especially for research reactor fuel, reduction of UF₄ is a possible route in the nuclear fuel cycle to produce metallic uranium. The production of uranium metal is a preliminary step to the manufacture of intermetallic U₃Si₂ and UMo alloys, which are the modern basis for manufacturing the nuclear fuel used in nuclear research reactors [1–4]. Metallic uranium is also necessary for manufacturing irradiation targets to produce ⁹⁹Mo by nuclear fission [5]. These targets are based on UAl_x-Al dispersion or thin foils of uranium metal [6–8]. IPEN-CNEN/SP has been nationalizing the nuclear fuel cycle for fuel and target fabrication [9,10].

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Among the UF₆ reconversion processes that are industrially established for the manufacture of nuclear fuel [11,12], the AUC route is the most attractive due to the good characteristics of uranium dioxide (UO₂) powder derived from AUC [13]. The aqueous process via AUC was developed in the early 1960s with the aim of reducing the number of processing steps involved in the aqueous process via ammonium diuranate; this process made it possible to obtain a precipitate with a low fluorine content that was very suitable for further processing [13–17]. In this process, the reaction of the gaseous compounds UF₆ (vapor), NH₃, and CO₂ and liquid water occurs. The obtained precipitate is approximately spherical in shape and has particle size large enough to impart a high flowability to the AUC powder. In a fluidized bed furnace, the AUC is decomposed to UO₃ and reduced to UO₂ using an atmosphere of H₂ and H₂O vapor. The UO₂ powder retains the original shape of the AUC, thus demonstrating a high flowability. The UO₂ powder produced from the AUC also has adequate sintering characteristics. For these reasons, this powder can skip the steps of grinding, precompaction, granulation, and sieving for pressing. For these reasons, this route is widely used for the manufacture of fuel for power reactors that use sintered UO₂ pellets. In addition, U₃O₈ can be obtained through the calcination of AUC. U₃O₈ can also be used as nuclear fuel for research reactors. Fig. 1 shows the UF₆ reconversion process via AUC to produce U₃O₈, metallic uranium, and U₃Si₂, which are the raw materials for manufacturing fuels and targets for research reactors.

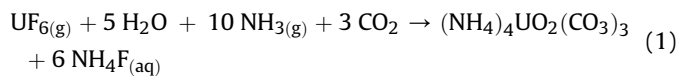
UF₄ is of great importance in nuclear fuel technology. It is an intermediate product for producing metallic uranium, which is important for U₃Si₂ and uranium target production for research reactors.

There are two conventional routes for producing UF₄. The first one employs the reaction of UO₂ powder with HF, which allows a reduction to metallic uranium. The other reduces uranium from UF₆ hydrolysis solution with stannous chloride or another reducing agent.

In order to minimize the loss of uranium in effluents and to recover as much uranium as possible, this work proposes a chemical process that aims to recover UF₄ from Filtrate III generated by the UF₆ reconversion process towards the AUC. Filtrate III is the effluent generated in the precipitation of ammonium peroxide fluorouranate (APOFU) from the treatment of the main filtrate of the AUC process, namely, Filtrate I (Fig. 1).

2. Materials and methods

The AUC precipitation is based in the following reaction:

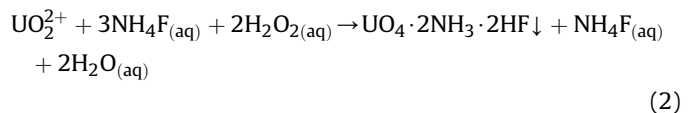


As shown in Fig. 1, in the AUC precipitation process through Eq. (1), two main effluents are produced: Filtrate I, from the first filtration of AUC, and Filtrate II, formed basically by ammonium bicarbonate solution (NH₄HCO₃), which returns to the AUC precipitation reactor for the processing of the next batch. A final washing with ethanol (H₅C₂OH), is performed to lower the moisture content.

The experimental procedures started with the APOFU precipitation from Filtrate I, which was the primary material used in this work. Filtrate I is formed mainly by an ammonium fluoride (NH₄F) solution with high concentrations of CO₃²⁻, NH₄⁺, and F⁻, and small amounts of uranium. After APOFU precipitation, the process to recover uranium had two main steps. The first was to obtain ammonium bifluoride (NH₄HF₂) from Filtrate III, which still contains uranium. The second step was fluoridation of UO₂ using the NH₄HF₂ and further decomposition to UF₄.

Table 1 shows the main chemical and physical characteristics of Filtrate I. For the uranium precipitation as APOFU, Filtrate I was heated to 95°C for 30 min with air flow and stirring for decarbonation. The carbonate ions were released as CO₂. After decarbonation was completed, the solution was cooled to 60°C and the remaining filtrate (NH₄F), now poor in carbonate ions, was treated with H₂O₂ 30%, which was slowly added with mechanical stirring and simultaneous bubbling of air and NH₃ to control the pH for precipitation. The pH was kept at 8.5.

From this treatment, APOFU was precipitated according to the reaction:

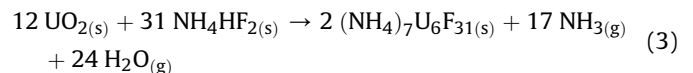


Much of the uranium contained in Filtrate I was recovered as APOFU. However, the remaining effluent (Filtrate III) still contained a significant concentration of uranium, approximately 2 mg/L; effluent was then treated to recover the remaining uranium as UF₄. Table 2 shows the main chemical and physical characteristics of Filtrate III.

Filtrate III was concentrated by heating at 95°C. The volume of the solution was reduced to about 25% of the initial volume. The NH₄HF₂ crystallized when this solution was cooled. The product was washed with ethyl alcohol to reduce humidity. This NH₄HF₂, containing uranium, was used to produce UF₄ from UO₂.

The experiments were carried out using as starting materials the NH₄HF₂ from Filtrate III and UO₂. This procedure is a possible alternative to the traditional route to produce UF₄ from UO₂ [18–20].

A two-step treatment was studied. For the first step, fluoridation was realized at 150°C, a temperature slightly higher than the melting temperature of NH₄HF₂ (124.6°C) [21]. This temperature is known to be sufficiently high for the reaction to occur. The water formed is easily released, avoiding the formation of UO₂F₂. The powders were blended with 20% excess of NH₄HF₂ relative to stoichiometry. The duration of the experiments for the first step varied between 2 hours and 24 hours. The process is based on the following reaction:



The second step of the process was the decomposition of (NH₄)₇U₆F₃₁, and takes place according to the following reaction:



For this step, the time was fixed at 2 hours and constant temperature of 500°C. These conditions were found by thermoanalysis to be adequate. The reaction was conducted under an inert atmosphere of argon (analytical Grade 5.0).

The yield of the fluoridation reaction [Eq. (3)] was monitored by amount determination of unreacted UO₂ present in the obtained UF₄. In the method to determine the residual UO₂ [22], the UO₂F₂ present in UF₄ was solubilized in ethanol and then separated by porous plate filtration. Uranium content was determined in this alcoholic solution. Once UO₂F₂ was extracted, the solid product (UF₄ + UO₂) was treated with ammonium oxalate and then filtered. At this stage, the UF₄ was dissolved and the uranium content was also determined in the solution. The remaining solid UO₂ was quantified by gravimetric analysis.

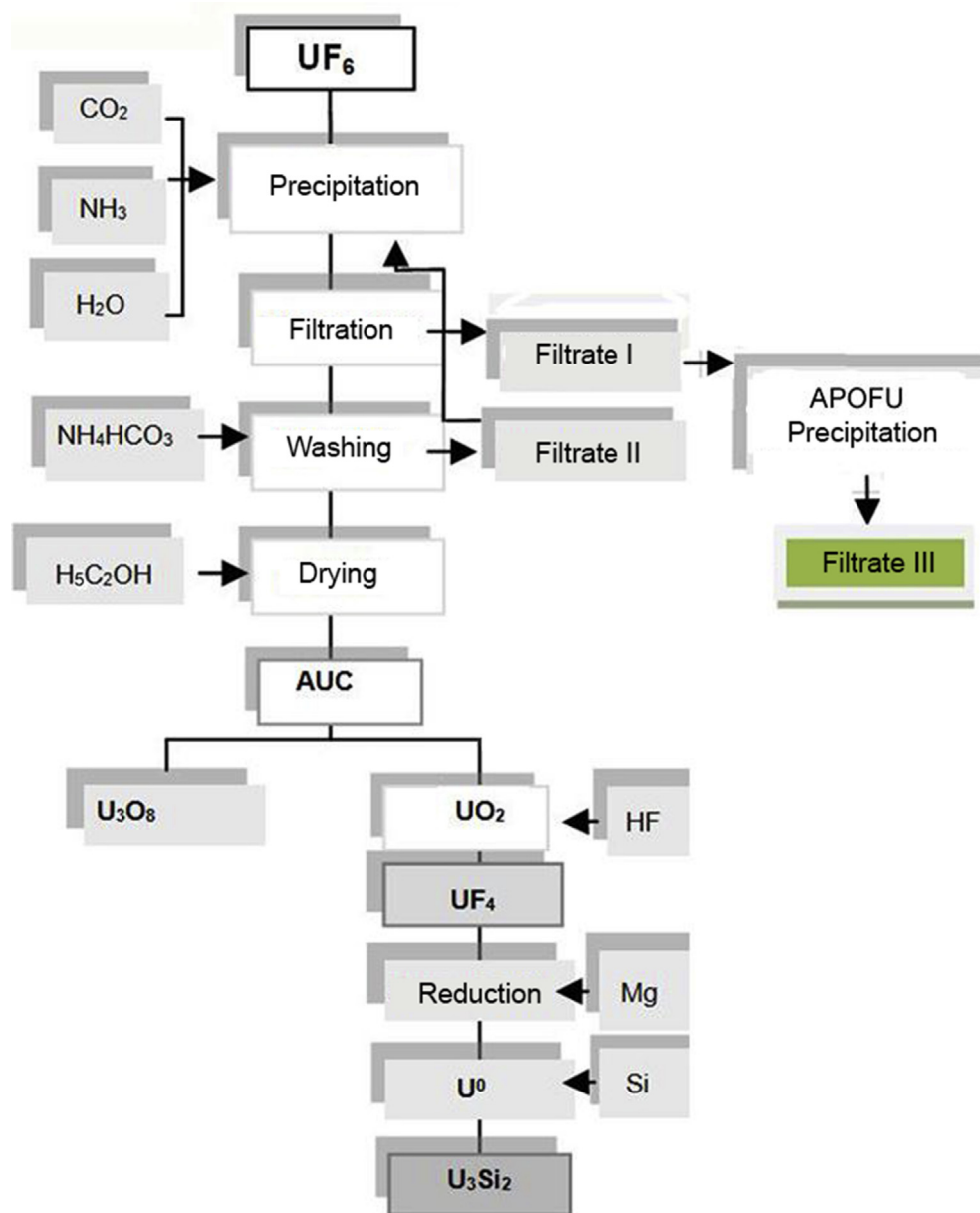


Fig. 1. Flowchart representing the UF₆ reconversion process via ammonium uranyl tricarbonate (AUC) to produce U₃O₈, metallic uranium, and U₃Si₂. Filtrate III is the effluent from which UF₄ is obtained. APOFU, ammonium peroxide fluorouranate.

Table 1
Physical and chemical properties of Filtrate I.

Ion	Mean concentration	Metallic impurities	µg/g
UO ₂ ²⁺	300 mg/L	Cd, Al, Mg, Mn	<2
CO ₃ ²⁻ +HCO ₃ ⁻	80 g/L	Ca, B, Zn, Mo	2.6
NH ₄ ⁺	110 g/L	Ni, Cu, Cr	10
F ⁻	100 g/L	Fe	10.5
Density	1.080 g/cm ³		
pH	9.0		

Table 2
Physical and chemical properties of Filtrate III.

Ion	Mean concentration
UO ₂ ²⁺	2 mg/L
NH ₄ ⁺	100 g/L
F ⁻	120 g/L
CO ₃ ²⁻ + HCO ₃ ⁻	4 g/L
Density	1.084 g/cm ³

3. Results and discussion

The crystallized NH₄HF₂ was characterized by X-ray diffraction (Fig. 2). The diffraction peaks of compounds NH₄HF₂ and NH₄F were identified. Despite the presence of a small amount of NH₄F, the route to prepare the NH₄HF₂ was found to be efficient.

After fluoridation of UO₂ with NH₄HF₂ [Eq. (3)], the resulting product was identified by X-ray diffraction as pure (NH₄)₇U₆F₃₁. Based on the literature that deals specifically with the dry route for obtaining UF₄ using NH₄HF₂ [23–25], NH₄UF₅ salt was expected to be obtained. However, the X-ray diffractograms did not show the presence of this salt, as can be seen in Fig. 3.

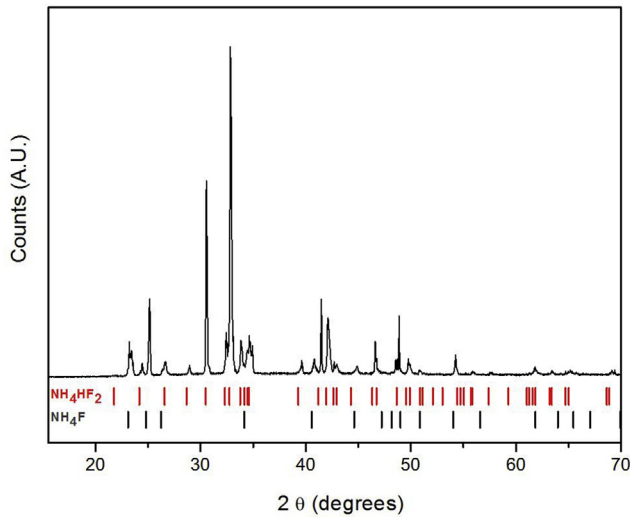


Fig. 2. X-ray diffraction pattern for the crystallized product from Filtrate III. Reference peaks of NH_4HF_2 and NH_4F were taken from PDF #12-0302 and #35-0758, respectively.

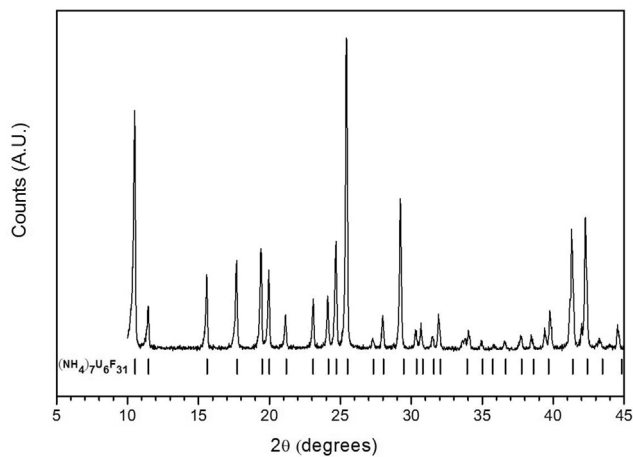


Fig. 3. X-ray diffraction pattern for the samples obtained after fluoridation of UO_2 [Eq. (3)]. Reference peaks of $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$ were taken from PDF 16-0756.

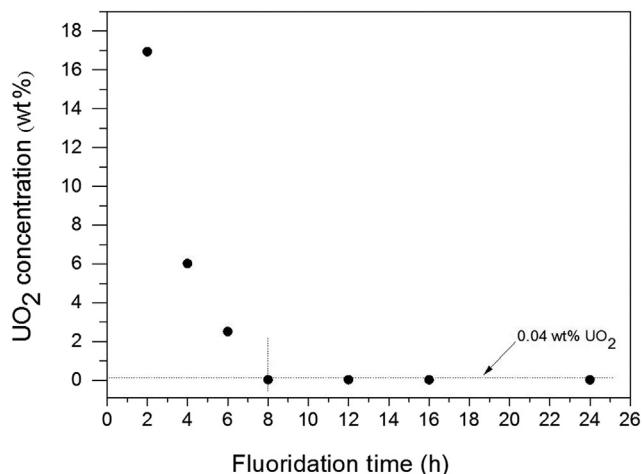


Fig. 4. Influence of time on fluoridation of UO_2 with ammonium bifluoride (NH_4HF_2).

The influence of time on the fluoridation of UO_2 is shown in Fig. 4. After 8 hours of fluoridation with NH_4HF_2 and subsequent decomposition [Eqs. (3) and (4)] the process was completed. Shorter fluoridation times resulted in UF_4 with high concentration of unconverted uranium oxides. Longer fluoridation times were found to be unnecessary. After 8 hours of reaction time, the yield of the reaction remains stable, with an average concentration of 0.04 wt% UO_2 in the UF_4 produced.

The temperature required for complete decomposition of $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$ to UF_4 [Eq. (4)] was confirmed by differential thermal analysis with simultaneous thermogravimetric analysis. The results are presented in Fig. 5.

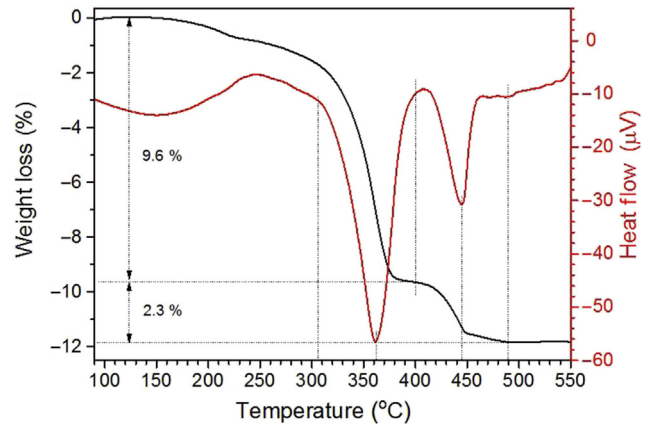


Fig. 5. Thermal analysis showing the decomposition of $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$ according to [Eq. (4)].

Table 3
Physical and chemical properties of UF_4 .

	UF_4 via SnCl_2 [26]	UF_4 this work
UF_4 (wt%)	99.85	98.69
UO_2F_2 (wt%)	0.34	1.27
UO_2 (wt%)	0.29	0.04
Loose bulk density (g/cm^3)	2.12	0.86
Tapped bulk density (g/cm^3)	2.65	1.19
Specific surface area (m^2/g)	0.21	2.85

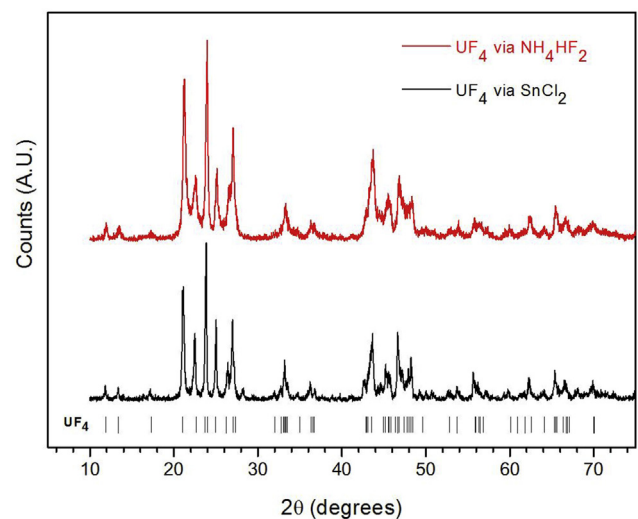


Fig. 6. X-ray diffractograms of UF_4 produced in this study and routinely produced at the Nuclear and Energy Research Institute (IPEN). Reference peaks of UF_4 were taken from PDF 71-1962.

As shown by the differential thermal analysis (DTA) curve presented in Fig. 5, the decomposition of $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$ is a two-step process. Up to 400°C, the primary mass loss is due to ammonia release of the system. Subsequently, up to 490°C, there is a secondary release of $\text{NH}_3 + \text{HF}$. The primary release event started at 306°C and then reached a maximum temperature of 360°C, and the secondary release began at 400°C and then reached a maximum temperature of 447°C. These results are comparable to those in the literature [20]. The decomposition was completed at 490°C, after the end of the second step. The total weight loss was 11.9 wt%, close to the theoretical value of 12.1 wt%, which indicates that mass release by decomposition reaction of $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$ was attained, leading to the formation of UF_4 . Temperature of 500°C and time of 2 hours were found to be adequate.

In this work, the physical and chemical properties of the UF_4 produced via NH_4HF_2 were compared with those of UF_4 routinely

produced at IPEN/CNEN-SP via SnCl_4 [26]. The results are presented in Table 3.

The reduction process that is routinely done at the IPEN/CNEN-SP tolerates up to 4 wt% of $\text{UO}_2 + \text{UO}_2\text{F}_2$ impurities. In this sense, the UF_4 obtained in this work meets the specifications. Additionally, the density of the UF_4 obtained in this study is relatively low; however, even though the density does seem to prejudice the following steps of the process, it would not be a problem, because the product would be diluted in UF_4 batches routinely produced. Moreover, the high specific surface area, more than 10 times greater than that of the routinely produced UF_4 , indicates a more reactive powder.

Fig. 6 presents X-ray diffractograms for UF_4 produced by both the method studied in this work and by the aqueous route, which is used in the routine production of fuel elements at IPEN/CNEN-SP. The diffraction patterns confirm the products as UF_4 . Fig. 7

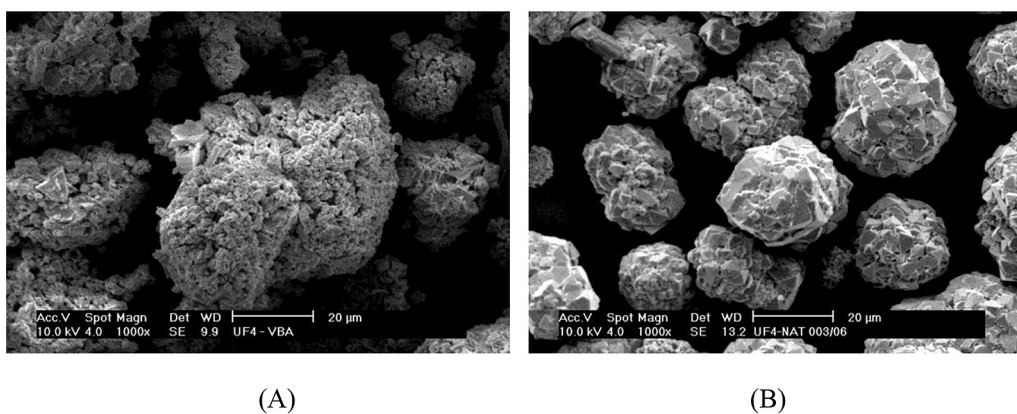


Fig. 7. Scanning electron microscopy (SEM) image of UF_4 particles. (A) Bifluoride route. (B) Via SnCl_2 .

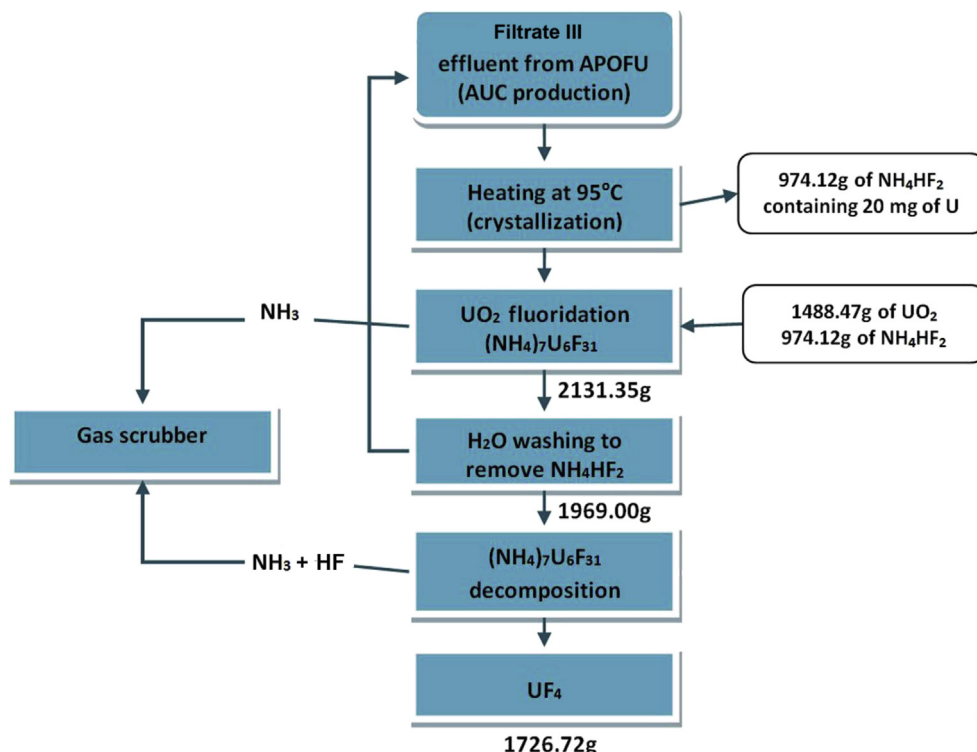


Fig. 8. Process for obtaining UF_4 from ammonium peroxide fluorouranate (APOFU) effluent. AUC, ammonium uranyl tricarbonate.

presents typical scanning electron microscopy images for the UF₄ powders produced routinely via the SnCl₂ route [26] and produced in this work, via the bifluoride route. The appearance of both powders is similar. They are presented as agglomerates of individual fine particles having a similar size. The sizes of the individual particles formed by the bifluoride route are slightly smaller than those produced by the SnCl₂ route. The agglomerates produced via bifluoride have noticeably greater porosity. This explains the lower densities and the greater specific surface area of this powder when compared to those characteristics of the powder produced via SnCl₂, as shown in Table 3.

Fig. 8 shows a process flow chart for the newly proposed procedure for producing UF₄ using fluoridation with NH₄HF₂ prepared from the APOFU effluent.

4. Conclusions

The process was fully tested by processing a batch with 1,488.5 g of UO₂. From this batch, 1,726.7 g of UF₄ was produced by fluoridation with NH₄HF₂. This result demonstrated a yield higher than 99% relative to the expected theoretical mass of UF₄ (1,731 g). The produced UF₄ showed adequate chemical and physical characteristics for its utilization as raw material for metallic uranium production.

The development of this process offers an efficient way to recover uranium and NH₄F from the reconversion process via AUC. The effluent generated is reduced and the yield for the production of metallic uranium, U₃Si₂, U₃O₈, and other uranium alloys for fuel fabrication is increased.

Conflicts of interest

All authors have no conflicts of interest to declare.

Acknowledgments

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