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ABSTRACT

The present work is focused on a study for the preparation of uranium tetrafluoride UF₄ appropriate for the metallic uranium (U⁰) reduction from solutions obtained by uranium hexafluoride (UF₆) hydrolysis using stannous chloride (SnCl₂) as the reducing agent.

The objective of the present study has been on one hand to gather experience within the uranium tetrafluoride preparation technology field by making use of an alternative, safe and simple process with which the knowledge obtained through uranium hexafluoride hydrolysis solution could be used, and on the other hand to determine the best conditions for obtaining this product, in view of the effect of experimental variables over the physical and chemical characteristics of the powder obtained, particularly the contents of uranium dioxide (UO₂), uranyl fluoride (UO₂F₂), the contents of hydrating water and specific surface, in order to make a correlation of those properties with the yielding of the reduction reaction caused by that compound at uranium metal producing. The metallurgical process for metallic uranium production is updated.

1. INTRODUCTION

The reactor IEA-R1 located in São Paulo, Brazil is a pool type research reactor which employs plate type fuel elements with using the dispersion of uranium compounds into aluminium. Within the nuclear fuel program necessary to meet requirements of the reactor IEA-R1, and also to support the Brazilian research development, a fuel element manufacturing program was started in 1984 using enriched uranium (19,95% w/w ²³⁵U) supplied by the United States Atomic Energy Commission.

As from 1992 the low reserve of uranium available, caused the development program to obtain ammonium diuranate (ADU) from hydrolyzed uranium hexafluoride solutions to be started.

As of 1994 such a procedure has been responsible for the continuation of the manufacture of fuel elements. That development has also enable data of major importance to be obtained aiming at the production of uranium tetrafluoride, and thus metallic uranium and its uranium silicide (U_3Si_2), within the modernization program of the reactor IEA-R1.

The uranium tetrafluoride (UF_4) plays a extremely relevant role within the nuclear fuel technology. It consists of an intermediary compound between the production of metallic uranium (U^0) and uranium hexafluoride (UF_6).

The UF_4 may be obtained by using several processes which are primarily divided into two main approaches: the dry way and aqueous way. Among these various processes for manufacture of UF_4 by the dry way, it should be cited the preparation by fluorination of UO_2 which comprises the reduction trioxide (UO_3) with anhydrous hydrogen at atmospheric pressure[3].

The first works aimed at obtaining UF_4 have been carried out through the aqueous way [1,2] by the end of the XIX century, and from an industrial standpoint they have prevailed up to the beginning of this century.

The processes essentially comprises the steps of reducing the uranium contained in uranyl fluoride solutions, uranyl chloride or uranyl sulfate up to its tetravalent state, and UF_4 precipitation by adding hydrofluoric acid.

With the development of dry way processes those previously made through na aqueous way have been given up because they presented difficulties associated with filtration, washing and drying. Even though abandoned, the processes using the aqueous via have never stopped calling the researchers attention of their simplicity and safety.

The present work describes the process for obtaining UF_4 by the wet way in UF_6 hydrolyzed solutions and comments on the evolution of a previous report about producing metallic uranium to obtain the alloy U_3Si_2 .

2. EXPERIMENTAL PROCEDURE

CHEMICAL PROCESS

For the production of UF_4 with a nuclear purity from UO_2F_2 acids solutions fundamental stages are required such as: obtaining the solution, reduction in the uranium valence and precipitation of the U-IV formed. These stages show a series of schematized operations as follows.

Obtaining UO_2F_2 solutions

Uranium hexafluoride is a crystalline substance at normal pressure and temperature conditions which when subject to a temperature of $90^\circ C$ under a pressure of 3kgf/cm^2 , and by means of an injecting nozzle, UF_6 gets in contact with the water thereby hydrolyzing instantaneously according to the reaction shown below.



The Table 1 shows the chemical characteristics of UO_2F_2 solution obtained from UF_6 hydrolysis.

Chemical Process

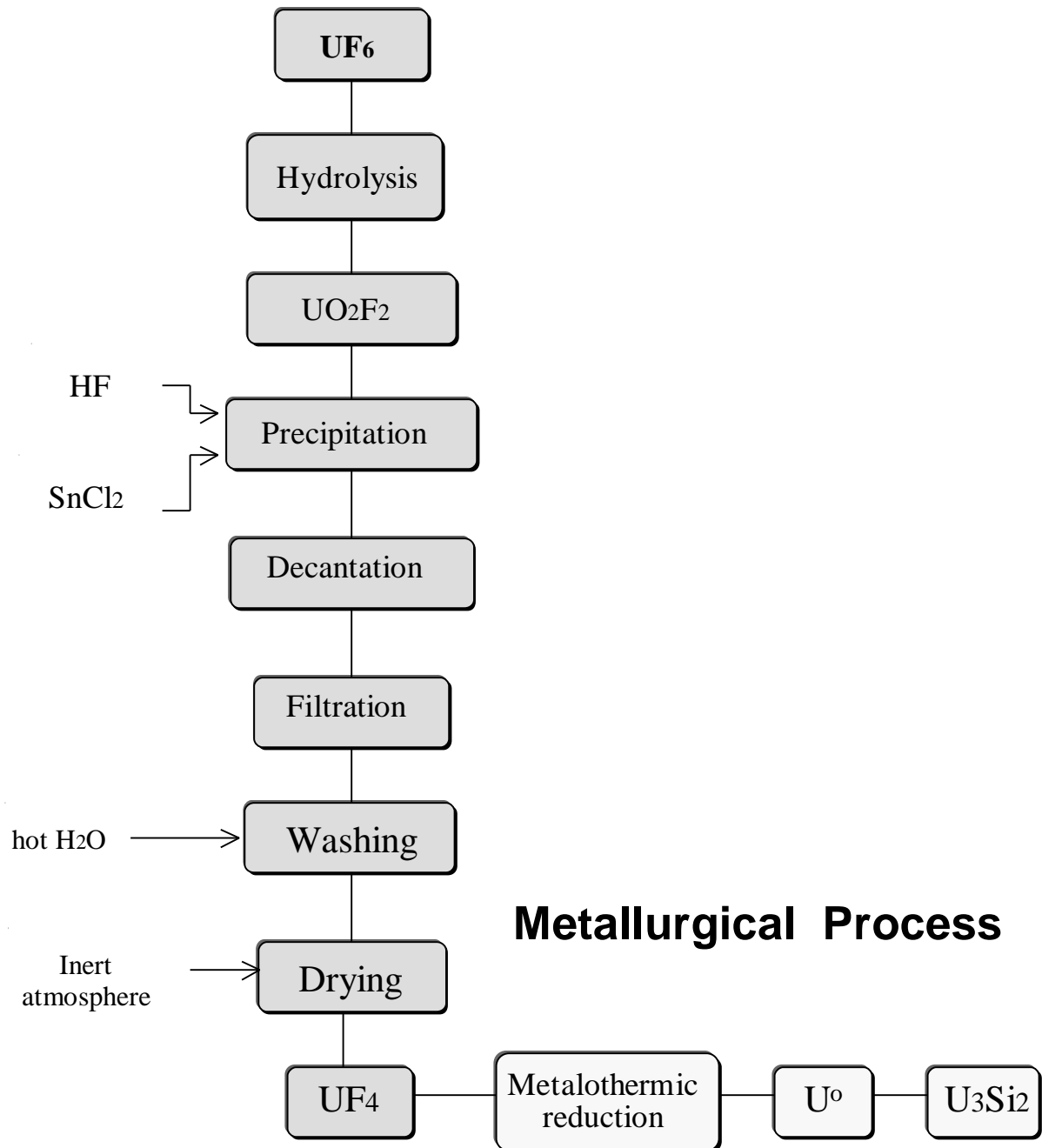


Figure 1 - Process to obtain UF₄

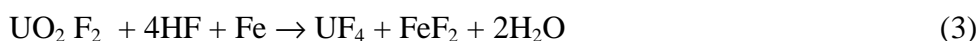
Table 1

Chemical characteristics of UO₂F₂ solution									
Uranium (g/L)		60							
Fluoride (g/L)		17							
Metallic impurities (µg/mL)									
Cd	B	P	Fe	Cr	Ni	Mo	Zn	Si	Al
<0.1	0.2	<100	1500	100	40	<2	100	300	40
Mn	Mg	Pb	Sn	Bi	V	Cu	Ba	Co	
10	15	<2	<2	<2	<3	3	1	<10	

Chemical Reduction

Uranium in its tetravalent state is very important in in different technological processes. Essentially, the preparation process by means of an aqueous way from solutions containing uranyl ion in its hexavalent state comprises its reduction up to the tetravalent state, and later precipitation as UF₄ by means of the HF solution. In aqueous solutions, these reductions are carried out through chemical, electrochemical or photochemical methods.

All the trials for the preparation of UF₄ using chemical reduction have been carried out using UO₂F₂ solution inside a stainless steel reactor, coated with teflon. The solution has been heated under continuous stirring to reach a temperature set, and the reducing agent has the been added. Next, the hydrofluoric acid (HF) precipitating agent solution has been slowly added. Tests have been carried out using some reducing agents, such: SnCl₂, CuCl, FeCl₂, Na₂S₂O₄.



Upon UF₄ precipitation, the suspension is left in rest up to reaching room temperature. After over 12 hours we have performed the solid/liquid separation by vacuum filtration, washing and drying in a muffle kiln.

We have studied the following parameters: reducing agent and uranium fluoride reaction and temperature of the precipitation for each of the reducing agents studied.

The salts obtained were all identified to uranium tetrafluoride. According to the results shown in Figure 2 we note that from reducing agents used only SnCl₂ and FeCl₂ have shown significant results as regards obtaining UF₄, but SnCl₂ is more consistent reducing agent at higher temperature. of process.

The influence of the temperature upon UO₂F₂ and UO₂ contents of the UF₄ obtained is shown in Figure 3. We have employed SnCl₂ as the reducing agent in this study in UO₂F₂ solution,

and drying of the residual moisture at 130°C. The content of Sn in all UF₄ obtained has shown to be in the range of 0.15 - 0,15%.

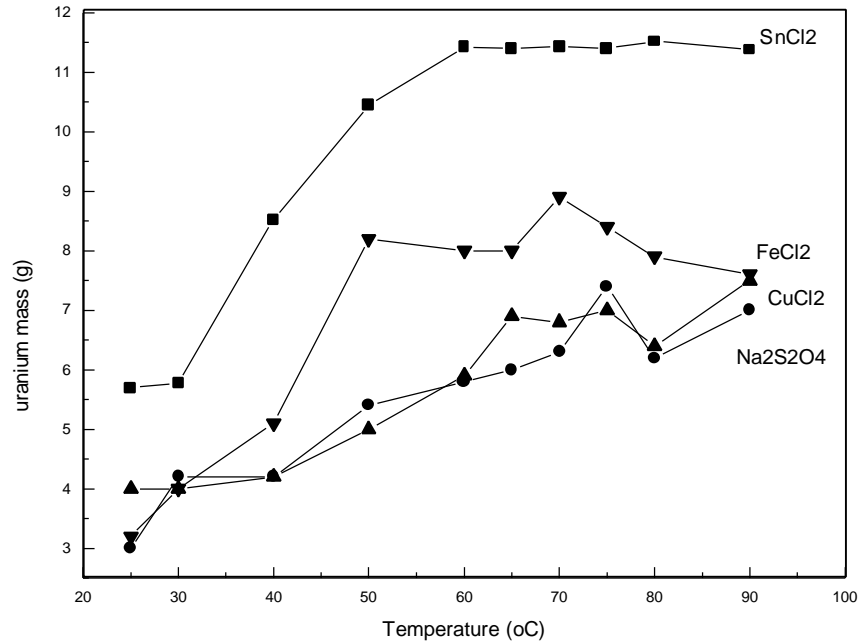


Figure 2 – Influence of reducing agent as a function of obtaining UF₄

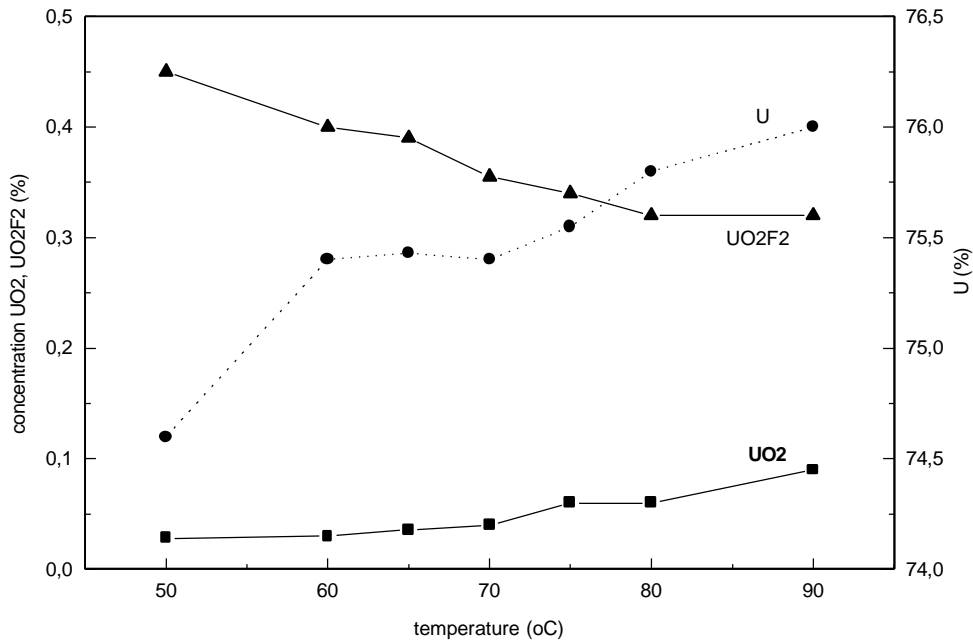


Figure 3 - Influence of temperature as a function of the contents of UO₂F₂ and UO₂ in UF₄

Obtaining UF₄

According to the results shown one can find that the process for obtaining UF₄ by reduction precipitation using SnCl₂ has shown the best results and achieved an UF₄ precipitation in the range of 98%. The precipitation with HF solution is relatively slow and tends to accelerate as the temperature



risers (1,2). This is important to avoid an excessive hydration of the precipitate and to facilitate the sedimentation, filtration and drying operations.

U-IV Precipitation

For the precipitation operation a reactor with a capacity of 50L provided with stirring and lining for heating with temperature controller has been required. The reactor has been built in stainless steel and coated with teflon having upper inlets for adding the reducing agent and the fluoridric acid solution. The discharge of the material produced is carried out through the equipment bottom part.

Decantation

After precipitation of U-IV all the material is transferred to a sedimentation tank where the UF_4 suspension is left to rest overnight. The sedimentary device comprises a cylindrical container having a conical bottom made of PVC. The sedimentary device has two outlets, one at the bottom to carry UF_4 up to the filter, and the other arranged at the lateral part to dispose mother liquors .

Filtration

The filtration process used to separate solid/liquid has been carried out using a vacuum filter system. The filtering mats employed are made of polyethylene fiber, a material which behaves efficiently with this kind of material.

Washing

This stage aims at removing some soluble UO_2F_2 and HF in excess present in UF_4 . Washing of UF_4 is carried out directly in the filter using distilled hot water (40°C) and the process does not change the contents of hydration water of the product, but simply leaves UF_4 free from UO_2F_2 and HF.

Drying

The drying operation whose purpose is to remove the residual water from the solid is carried out in electric 1000W power stoves with air forced recirculation system. The material obtained is placed in rectangular aluminium trays coated with teflon. The temperature is maintained around 130°C for 12 hours by means of the automatic control. The drying temperature should not be higher than that indicated as there is no atmosphere control, in other words the oxygen in the air may produce UO_2F_2 which absorbs the water and causes an effect contrary to that desired as UF_4 is dried at temperatures higher than 300°C.

Dehydration

The dehydration of hydrated UF_4 is further complicated by the extreme sensitivity of the system to trace oxygen. The dehydration process should be long enough and should even allow traces of oxygen to be allowed access to the UF_4 , oxidation to uranyl fluoride will occur. It should be remarked that satisfactory results have already been obtained by using inert atmosphere drying at 400°C.

Physical - Chemical Properties of Uranium Tetrafluoride

During the uranium processing stages, the goal is to achieve an end product with high purity and showing physical and chemical characteristics appropriate for the preparation of nuclear fuel.

Table 2 lists the suitable chemical and physical characteristics of UF₄ for a later reduction of the metallic uranium.

Table 2: Chemical and Physical Properties of UF₄ produced by an aqueous via								
	at 130°C	inert atmosphere at 400°C						
Uranium (%)	74.20	75.60						
Fluoride (%)	24.60	27.90						
UF ₄ (%)	97.50	99.85						
UO ₂ F ₂ (%)	0.29	0.34						
UO ₂ (%)	0.06	0.29						
HF(%)	0.23	0.12						
Moisture (%)	0.33	< 0.03						
Hydration H ₂ O (%)	4.50	< 1.00						
Metallic Impurities (µg/g)	Fe	Cr	Ni	Mo	Al	Mn	Cu	Sn (%)
	<20	<10	<10	<5	<10	<5	<5	0.1
Density (g/cm ³)	6,70							
Granulometry (µm)	15,00							
Specific Surface (m ² /g)	0.21							

Characterization of the Product as UF₄

For the characterization of the product as UF₄, diffractometric x-ray analysis and electronic scanning microscopy technique are used. The x-ray diffractogram is typical representation, of a common use UF₄ product.

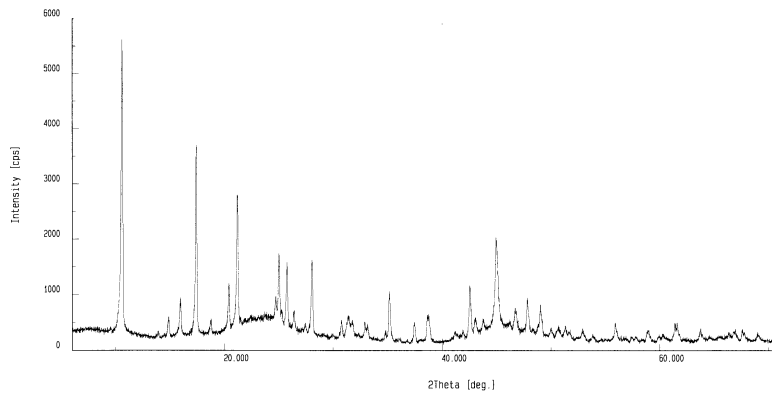


Figure 4 - X-ray diffractogram of UF₄

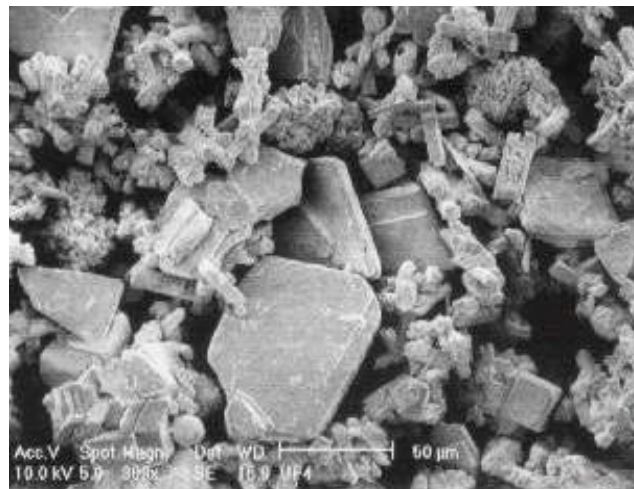


Figure 5 - Picture (MEV) showing UF₄ crystals
METALLURGICAL PROCESS UPDATED

As reported in a previous paper [4] presented in RERTR/97, we shall update the following points:

- The metalothermic reduction of uranium previously stated as being carried out by magnesium, shall be modified towards calcium, since a better yield is envisaged for a critical mass production (<4kg). Calcium is thermodynamically more active reductant than magnesium, but many other concerns arise, because the handling of calcium should be made under proper facilities and protection means. For this, a new project for this plant is taking place nowadays, aiming at starting some production of uranium by the next year. All experiments made by magnesiothermic route has been ceased .
- Some experiments on ignitor for calcium bombs, are being presently worked out, without anything to reported yet.

3. CONCLUSIONS

According to the results obtained we could find that the present suggested route to obtain UF₄ by chemical reduction and precipitation is a simple process which enables to achieve a quantitative recovery of uranium amounts.

The present work has shown that the process is perfectly feasible to prepare UF₄ by an aqueous means using SnCl₂ as the reducing agent with the requirements necessary to meet the manufacture of metallic uranium.

It has been found to be evident that the process has advantages in respect to the others, and it should be mentioned that UF₄ may be obtained using simple and low cost equipment.

UF₄ may be obtained in safer conditions for the operators, as the fluoridric acid solutions are potentially less dangerous than the hydrogen fluoride.

We should point out that the product (UF₄) will likely be tried shortly as a raw matter for the preparation of metallic uranium.

4. REFERENCES

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