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PROCESSES TO OBTAIN METALLIC URANIUM FROM UF₆

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ABSTRACT

This paper presents the developed work with the aim to obtain a conversion process from UF₆ to metallic uranium. The UF₆ cannot be converted directly to U metal, therefore needs the path through intermediate compounds, as the UF₄, existing several alternative routes. Many processes were studied, finally defining the optimum route: (1) Hydrolysis of UF₆ (to transform it to UO₂F₂ solution); (2) Reduction of UO₂F₂ (with SnCl₂ and HF) to precipitate UF₄; and (3) Reduction of UF₄ with magnesium to obtain of metallic Uranium.

The work included experimental tests with natural uranium, a study of the process variables and the design of the equipment. Because the work was done with enriched material, special attention was paid to operational radiation safety protocols, due the risk of contamination and critical mass, which was considered in the design of equipment and processes. To work at subcritical condition implied batch operations. Once optimized the equipments and defined the process variables, the conversion of 73 kilos of UF₆ enriched to 19,75 % (LEU) was realized, obtaining 42 kilos of metallic uranium, with a 85.1% efficiency.

INTRODUCTION

CCHEN had 73,8 Kg of UF₆, of low enrichment, LEU, from the Popular Republic China. In the Conversion Laboratory of the Nuclear Materials Department, several alternative routes were explored for the conversion of enriched UF₆ to obtain metallic uranium, and thus, provide raw material to CCHEN's Fuel Elements Fabrication Plant, whose facilities are made at productive level, fuel elements for research reactors, using metallic uranium LEU as raw material.

The activities of research and development were separated into two stages, according to the sequential processes leading to metallic uranium, as shown in Figure N° 1:

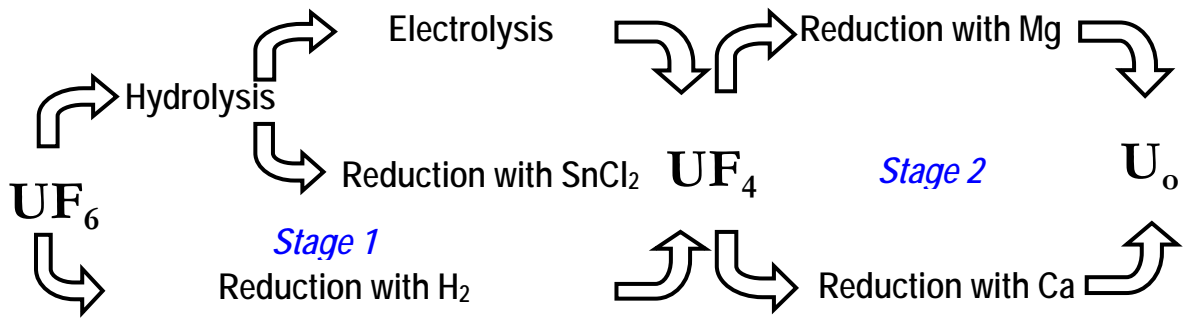


Figure N° 1: Processes studied to select the optimal route [1]

After years of study, it was found that the best route for an efficient, economical and safe conversion is the following: hydrolysis of UF_6 to obtain a UO_2F_2 solution, following for the reduction of UO_2F_2 and precipitation of UF_4 by the addition of $SnCl_2$, and finally a magnesiumthermic process to obtain U metal (Figure N° 2).

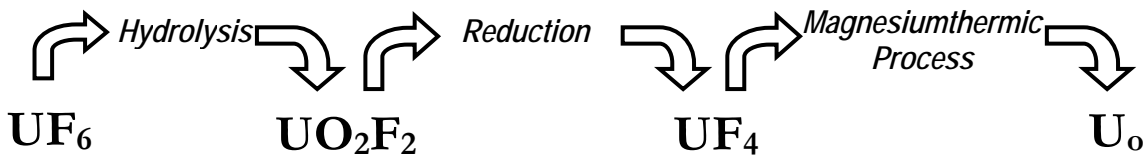
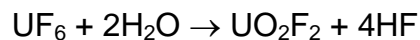


Figure N° 2: Finally selected Processes

DEVELOPED PROCESSES

a) Hydrolysis

At room temperature the uranium hexafluoride is a solid, and is required to increase the temperature above $56^\circ C$, to sublimate the solid and that way, achieve an increase in the pressure inside the container, allowing the gas to come out and can be lead through Monel 400 pipes, using N_2 as a carrier gas. The gas mixture enters the hydrolysis reactor (Figure N° 3) which is contacted with a water mist, reacting according to the equation:



Working with enriched material, the condition of subcriticality must be kept, which forces to work in batch and with a volume and concentration of uranium in the liquid solution very well definite, 20 liters and 85-95 gU/l maximum.

Due to the risks of toxicity of the UF_6 , and the formation of HF in contact with humidity, it is necessary that the equipment is confined and depressed. Because of that, a cabin was designed and constructed with a constant extraction, in order to assure a depression, with an exterior gas scrubber system.

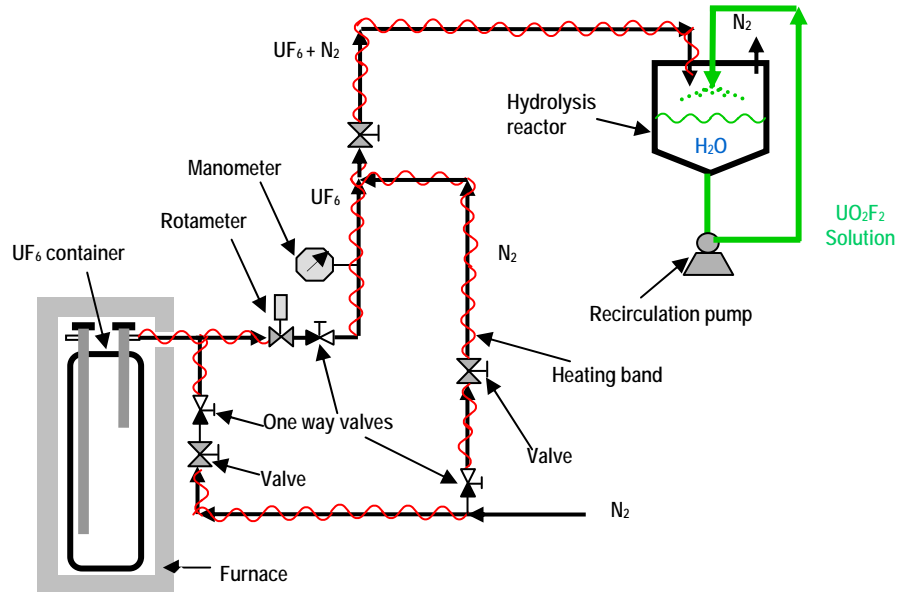


Figure N° 3: Schematic of the hydrolysis system

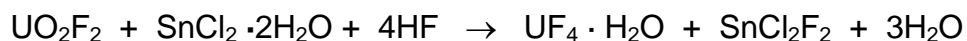
The process parameters studied to obtain the UO_2F_2 solution with the concentration already mentioned, were heating temperature of the UF_6 gas, heating temperature of the pipes and the carrier gas N_2 flow. It was indispensable to determine the solution concentration before deciding the end of the batch, due to the possibility that critical mass could be reached. This was solved by means of an indirect method using a radiation detector, measuring always in the same point of the hydrolysis reactor and then constructing a graph Counts/s v/s solution concentration (Figure N° 4). During the processing, the flow of UF_6 decreased from 3 to about 10 g U / min, due to the progressively smaller mass of gas inside the cylinder, producing a lower internal pressure.

At the hydrolysis process, 73 Kg of UF_6 were processed, corresponding to 49,4 Kg of U as UO_2F_2 solution, with a yield of 99,9 %. At this stage of the process generates no loss, by-products or waste.

b) Reduction

The second stage was carried out introducing to the reactor a solution of uranyl fluoride, UO_2F_2 , with the addition of the reactants SnCl_2 and HF [2].

The following reaction takes place:



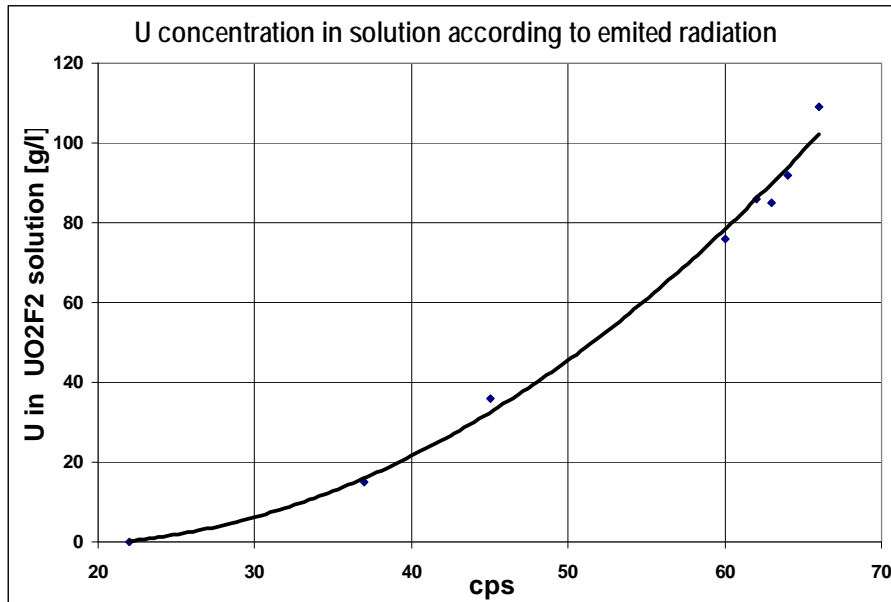


Figure N° 4: Counts/s v/s Concentration of solution UO₂F₂ in gU/l

The reactants HF and SnCl₂ were used in excess, for assuring the complete reaction of the UO₂F₂. The addition of the reagents into the reactor was produced with a slight and permanent agitation and an application of temperature (Figure N° 5). Temperatures and process times were decided. The products of this reaction appear in 2 phases, a solid one and a liquid one. The solid phase corresponds to the hydrated UF₄ and the liquid one is composed by the soluble salt SnCl₂F₂, water and excess HF that constitutes the supernatant. The solid phase was filtered and undergoes to successive washes to eliminate remains of the reactants, then it is dried and dehydrated in a protective atmosphere of Ar. Special care must be taken because the material is in the shape of fine powder.

The particle size range of the UF₄ goes from 0,4 to 50 μm, with 10 % under 11 μm, 50 % under 8 μm and 100 % under 50 μm. To know the morphology obtained UF₄, was performed SEM, to dry and without dehydration samples, as well as dehydrated in Ar atmosphere samples. In the micrographies of the Figure N° 6 a slight difference is observed in the surface of the particles. The dry sample shows particles with a lightly rough surface, not like those that were dehydrated, which can be seen with a smoother surface and a more definite cubic form.

In the precipitation of UF₄, were obtained 63 Kg of dehydrated UF₄, with a performance of 97.02 %. At this stage, the by-products produced were wash water and supernatant, with uranium contents of 202 mg U/lit and 540 mg U/lit respectively, which could be recovered for further processing.

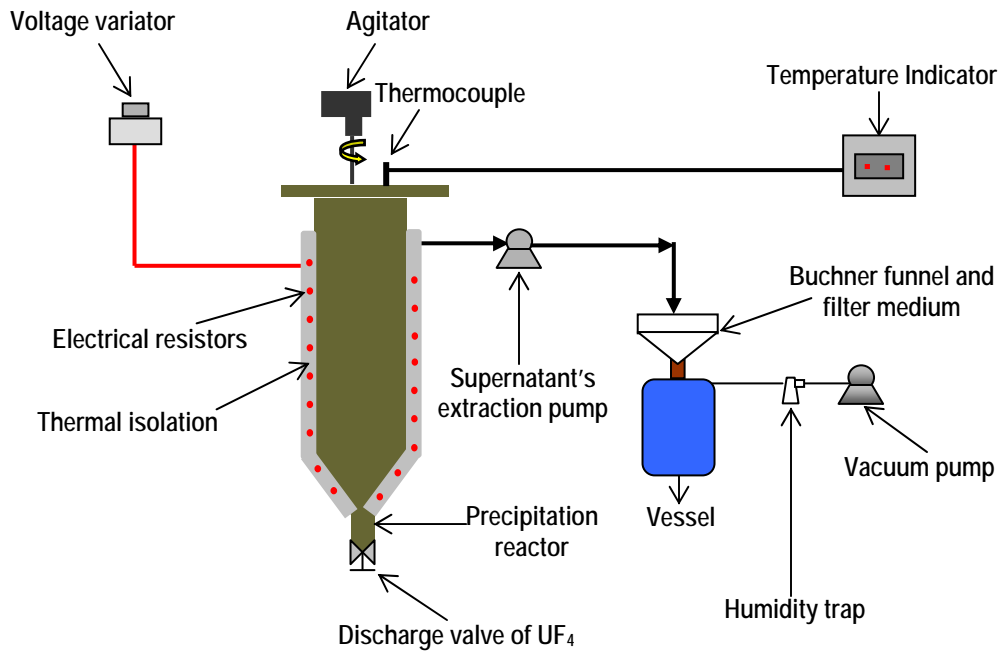
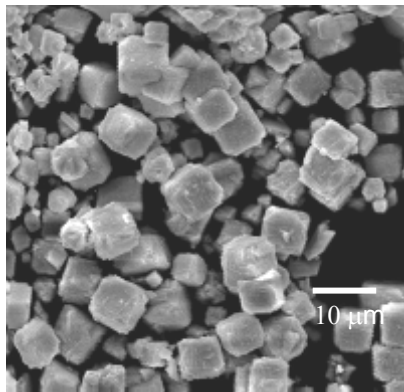
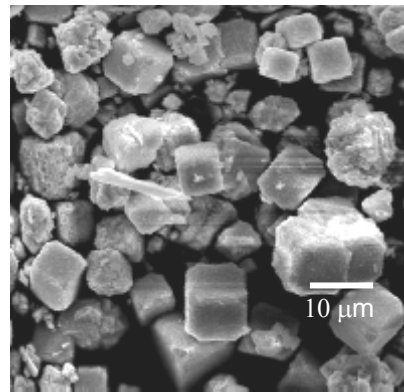


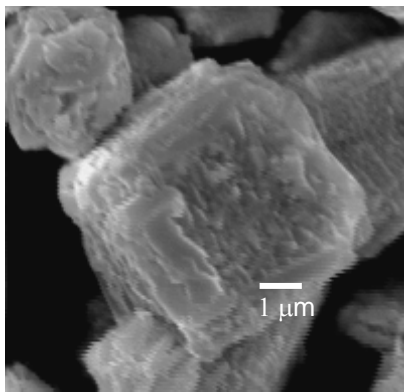
Figure N° 5: Schematic of precipitator system



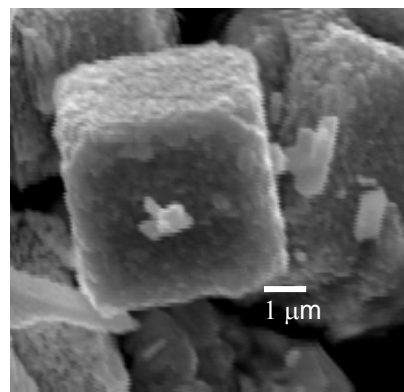
(a) UF_4 drying at 100 °C



(b) UF_4 drying at 100 °C and dehydrated at 400 °C in Ar atmosphere



(c) UF_4 drying at 100 °C

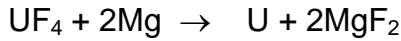


(d) UF_4 drying at 100 °C and dehydrated at 400 °C in Ar atmosphere

Figure N° 6: Micrographies of obtained UF_4 by Scanning Electronic Microscopy, SEM

c) Magnesiumthermic Process

The process consists of producing the reaction:



The process begins with mixing, Mg powder and UF_4 previously dried and dehydrated. Then the whole mix is introduced in a graphite crucible and compacted to achieve an intimate mixture of the components that provide a better thermal homogeneity and therefore a better efficiency of the reaction. Due to considerations of critical mass, the work was realized in batch operations, with loads of UF_4 in order of 7 Kg [3].

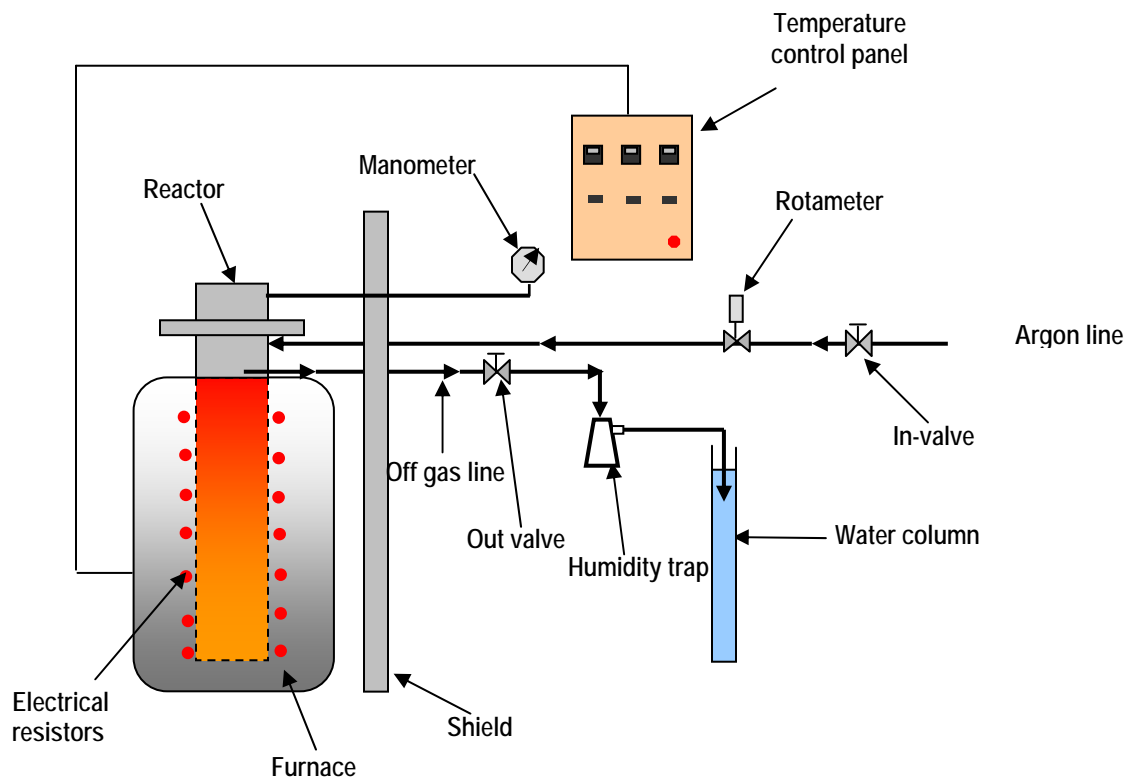


Figure N ° 7: Schematic of magnesiumthermic process system

To initiate the reaction, is required to preheat the load, using a furnace, over the spontaneous ignition temperature 500°C (Figure N° 7). This preheating is also necessary to ensure the evacuation of volatile components prior the reaction, thus avoid an increase of the interior pressure of the reactor. The evacuation is achieved using a low flow of argon, which also acts as a protective atmosphere to avoid oxidation. The function of the water column is to maintain a certain level of overpressure of argon to prevent possible entry of air and ensure that the reactants do not oxidize.

When the temperature has reached a level near to reaction temperature, the reactor is sealed. The reaction is highly exothermic producing an increase of temperature over 1400 °C in a few seconds and then the products uranium and magnesium fluoride, both in liquid state, are separated by density, 19 and 3,3 respectively.

In the final stage of the magnesiumthermic process, 42 Kg of U was obtained in the ingots, with an average yield of this process of 87.8 %. This efficiency could have been better, but in some operations there was a displacement of the thermocouple of control, and the reaction took place with thermal heterogeneity in the load reducing the performance. As by-product, 34 Kg of slag was obtained, principally MgF₂, with a uranium content of 15 %.

CONCLUSIONS

- The chemical characterization of the product U accomplish with the normative institutional requirements for its use in nuclear fuels for research reactors.
- The global yield of the conversion of UF₆ to U metal slightly exceeded 85 %.
- The overall balance of mass shows that the by-products of the processes have 6,3 Kg of U, that is possible to recover, developing the pertinent processes.
- The Institution has developed a process of Conversion of UF₆ to metallic Uranium that consists of three stages: - Hydrolysis of UF₆ to obtain UO₂F₂ solution - Precipitation of UF₄ by reduction of the UO₂F₂ using SnCl₂ and HF - Obtaining of metallic uranium by reduction of UF₄ by a magnesiumthermic process.
- The CCHEN has this process operative, in an installation that fulfills the international requirements, with processes with operating license, and a quality management system under ISO Norm 9001.

This development is another step in the fuel cycle stages, and will be completed with the recovery of uranium from materials derived from the processes outlined in this work, as derived materials from the process of fabrication of fuel elements.

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- [3] W. Donoso, P. Rojas, A. Garrao, L. Catalán, H. Contreras, "Desarrollo del proceso de obtención de uranio metálico a partir de UF₄, mediante metalotermia, empleando magnesio como reductor", CONAMET/SAM – SIMPOSIO MATERIA, Santiago, Chile, Noviembre 2002.