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# RECOVERY AND ENRICHMENT REDUCTION OF HIGHLY ENRICHED URANIUM CONTAINED IN A URANIUM HEXAFLUORIDE CYLINDER

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## ABSTRACT

In the context of project UBERA-6 (Low Enrichment Uranium for the Argentinean Reactor -06) the Nuclear Materials and Fuels Activity Unit of the Argentinean National Atomic Energy Commission (CNEA), has developed and carried out a process for the recovery and subsequent enrichment reduction of 90%-enriched uranium in the form of partially hydrolyzed uranium hexafluoride, contained in a 5A cylinder with blocked valves. The process consists of several steps: the opening of the cylinder, hydrolysis and dissolution of the uranium, precipitation with ammonium hydroxide solution, re-dissolution with nitric acid, enrichment reduction and purification by solvent extraction. The method used allowed an efficient operation, with the recovery of 95.1% of the uranium contained in the cylinder. The obtained uranium solution, with an enrichment of less than 20%, is suitable for the manufacture of fuel elements for research reactors and radioisotope production.

## 1. Introduction

In fulfillment of an agreement between the Argentinean National Atomic Energy Commission (CNEA) and DoE, and in the frame of the RERTR program, the LTA nuclear facility, which belongs to the Nuclear Materials and Fuels Activity Unit of CNEA, has developed and carried out processes for the recovery and subsequent enrichment reduction of 90%-enriched uranium contained in different types of scrap. One of those processes implied the recovery of highly enriched uranium in the form of partially hydrolyzed uranium hexafluoride, contained in 5A cylinder with blocked valves.
Since 1990, the LTA facility has been playing a role in the production of MTR fuel elements and irradiation targets for Mo-99 production. The recovery of scrap generated at the different stages of the manufacture of fuel elements, performed by

LTA, permits a reduction in the non-operative inventory. This improves the safeguards for the existing nuclear material in the LEU fuel cycle.
The LTA has acquired considerable experience in chemical processes for the recovery and purification to nuclear grade of non-irradiated, low-enriched uranium from different types of compound (scrap). The facility has also processed scrap containing HEU (90%), but in that case only the recovery step was applied.
The recovery of uranium from UF6 required the modification of the installation and the update of the documentation in order to obtain the start-up and operation licenses. It was necessary to design, build and assemble special equipment, such as a glove box for handling the 5A cylinder, a cooling system and a vessel for isotopic dilution of the uranium.

## 2. Process description

In the preliminary analysis of the process it was considered that the blockage of the cylinder valves was probably due to the presence of uranyl fluoride produced by (total or partial) hydrolysis of the uranium hexafluoride. X-ray images were taken in order to know the distribution of nuclear material inside the cylinder and also to verify its physical integrity. X-rays showed that:

- Most of the material was at the bottom of the cylinder.
- Cylinder integrity was satisfactory.
- There was some material in the pipes below the valves.

The selected process involved the following steps (Figure 1):

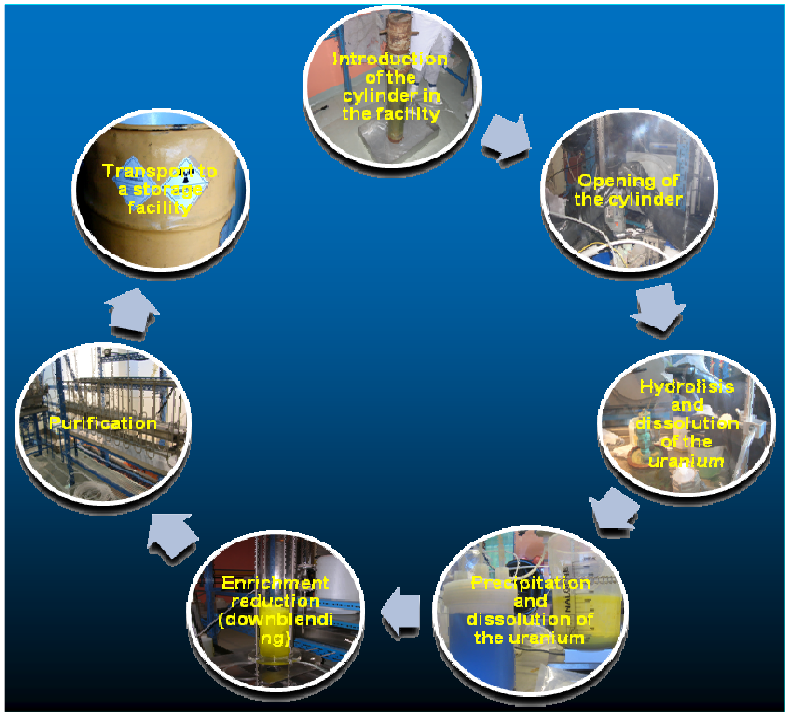
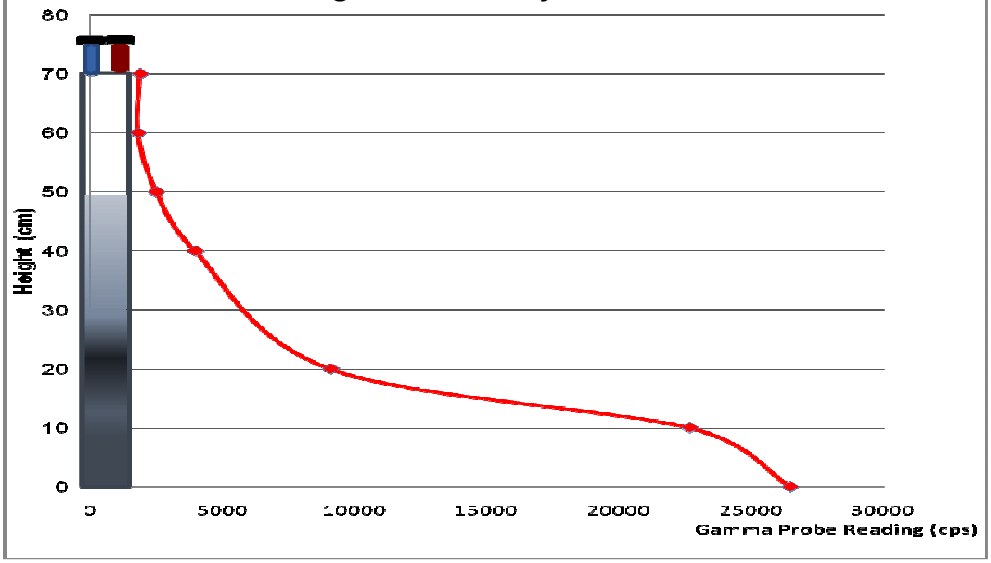



Figure 1 - Process steps

Once the facility passed the radioprotection tests and the operation was authorized, work with nuclear material began.

First, uranyl nitrate solutions were prepared with natural uranium. These solutions were analyzed to quantify their uranium concentration and kept for later use in the downblending stage.
After the UF6 cylinder was introduced in the facility, a gamma-ray emission profile was obtained (see Figure 2). The profile confirmed the X-rays results regarding the distribution of the uranium (mostly at the bottom of the cylinder).

**Figure 2 - UF6 cylinder**




Afterwards, the following steps were taken:

*Stage 1*: *Opening of the UF6 cylinder*

The purpose of this stage was to get access to the cylinder interior, avoiding leaks of uranium compounds. To this end, the following steps were performed:

- Decontamination and cleaning of the cylinder external surface.
- Cutting and removal of the cylinder cap and introduction of the cylinder in the glove box.
- Cooling of the cylinder contents by liquid nitrogen fed to a jacket surrounding the cylinder. This step was carried on to ensure that, if any UF6 was still present in the cylinder, it would remain mostly in solid form, with a very low vapor pressure.
- Drilling of the cylinder top. A portable drilling machine was used

*Stage 2: Hydrolysis of the uranium hexafluoride and dissolution of the uranyl fluoride*

The objective of this stage was twofold: to achieve the hydrolysis of the uranium hexafluoride that could still exist in the cylinder and to dissolve the uranyl fluoride. The following steps were taken:

- Addition of deionized water and interruption of the cooling. The cylinder was allowed to warm up until it reached room temperature. In this step the following chemical reaction proceeded:

$$UF_{6(s)} + 2H_2O_{(l)} \rightarrow UO_2F_{2(aq)} + 4HF_{(aq)}$$

- Split of the resulting solution in three fractions for nuclear safety reasons. All subsequent operations were carried out with $^{235}U$ masses under 250g.
- Scrubbing of the cylinder with multiple volumes of 15% (w/w) nitric acid solution, and, finally, with an 5% (w/w) ammonium carbonate solution, in order to remove as much uranium as possible from the cylinder. The progress of the scrubbing was verified by measurements with a gamma probe, as shown in Figure 3. In the last measurements no significant variations in the probe readings were found.

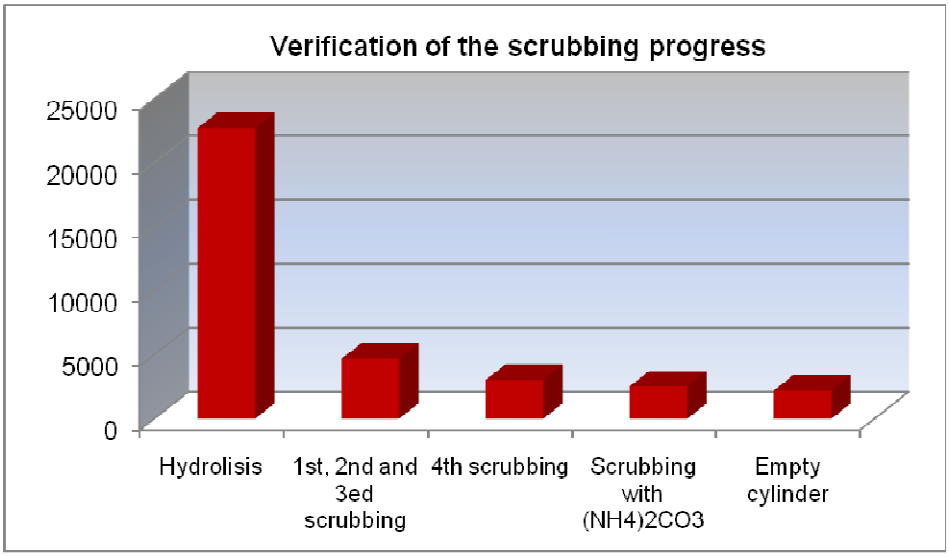



Figure 3: Verification of the scrubbing progress with a gamma probe.

*Stage 3: Precipitation and re-dissolution of the uranium*

This stage aimed at removing the fluoride from the uranium solution, as the following processes would be carried out in nitric acid media using stainless steel equipment. The steps were:

- Each solution was weighed and sampled, and the uranium was precipitated by addition of ammonium hydroxide. The precipitate was filtered and washed with diluted ammonia.

$$2UO_2F_{2(aq)} + 6NH_4OH_{(aq)} \rightarrow (NH_4)_2U_2O_{7(s)} + 4NH_4F_{(aq)} + 3H_2O$$

- The ammonium diuranate precipitate was dissolved with an excess of nitric acid. A

solution of uranyl nitrate with a 3 M concentration of free nitric acid was obtained.

$$(NH_4)_2U_2O_{7(s)} + 6HNO_{3(aq)} \rightarrow 2UO_2(NO_3)_{2(aq)} + 2NH_4NO_{3(aq)} + 3H_2O$$

- The resulting solution was weighed and sampled in order to analyze its uranium concentration and isotopic composition. The latter was measured by TIMS and ICP-MS.

*Stage 4: Enrichment reduction*

Enrichment reduction was achieved by mixing solutions of the same chemical species. The uranyl nitrate solution containing 90%-enriched uranium was mixed with a uranyl nitrate solution prepared with natural uranium. A special vessel was designed and built for this operation. It has a cylindrical shape, with a diameter smaller than the critical diameter for U-90%. The obtained solution was sampled to measure its isotopy. Final enrichment had to be between 19,55 and 19,95 % in $^{235}U$ to be suitable for the manufacture of new fuel elements.

*Stage 5: Purification by solvent extraction*

The low-enriched uranium (LEU) solution obtained in the previous stage was contaminated by impurities from the UF6 cylinder and from the reagents employed. Thus it was necessary to purify it in order to comply with the specifications for nuclear fuel elements. A scheme of the purification process is shown in Figure 4.

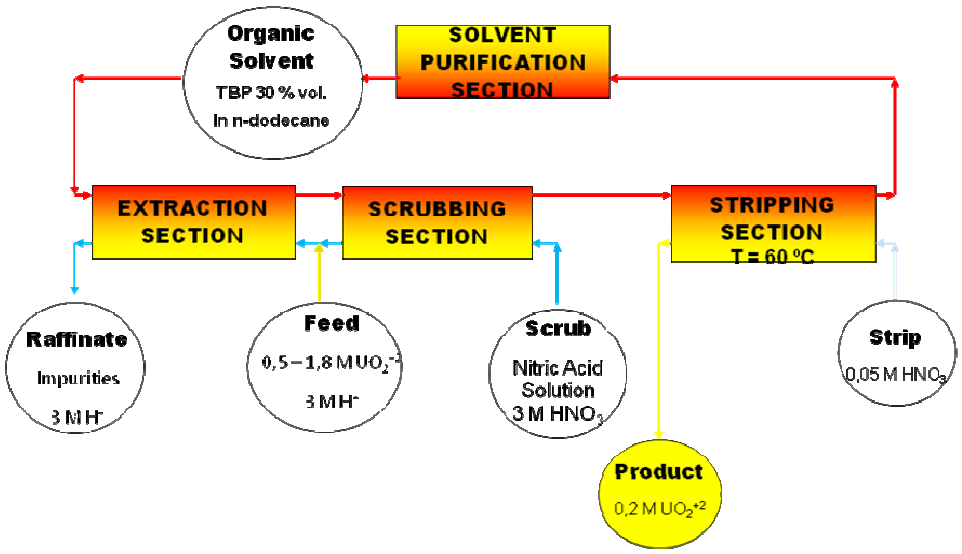



Figure 4: Purification of uranium by solvent extraction.

The process was based on a liquid solvent extraction operation using a mixture of tributyl phosphate (TBP) and dodecane as solvent. After the extraction, scrubbing and re-extraction stages, a nuclear grade uranyl nitrate solution was obtained. A typical analysis of the product solution is shown in Table 1.

| Element | Concentration ($\mu g.\ g^{-1}$ U) |
|---|---|
| Al(μ) | <1 |
| B | <0.5 |
| Cd | <0.5 |
| Ca | 85±4 |
| Cu | <2 |
| Cr | <2 |
| Fe | 15±1 |
| Mg | <10 |
| Mn | <10 |
| Mo | <2 |
| Ni | <2 |
| Be | <2 |
| Zr | <2 |
| Co | <2 |
| Li | <2 |
| Hf | <2 |
| W | <2 |
| Dy+Eu+Gd+Sm | <2 |

Table 1- Typical analysis results

*Stage 6: Transport of the product to a storage facility*

The product was sent to a storage facility, to be stored until it is required for the manufacture of nuclear fuel elements for research and radioisotope production reactors. An AF-type package was used.

## 3. Results

The results obtained with the described process are shown in Table 2.

| | IDENTIFICATION | HEU MASS g | U235 MASS g | PARTIAL PERCENT % | TOTAL PERCENT % |
|---|---|---|---|---|---|
| | 5A CYLINDER DECLARED VALUES | 649.3 | 585.29 | | 100 |
| TOTAL RECOVERY | Total HEU Downblended | 602.72 | 543.41 | 92.8 | 95.1 |
| | Samples | 15.05 | 13.57 | 2.3 | |
| TOTAL WASTE | Solid waste | 0.80 | 0.72 | 0.1 | 3.2 |
| | Treated cylinder | 12 | 10.82 | 1.9 | |
| | Analythical waste | 2.26 | 2.04 | 0.4 | |
| | supernate and wash from precipitates | 5.46 | 4.92 | 0.8 | |
| TOTAL ACCOUNTED | | 638.29 | 575.48 | | 98.3 |
| MATERIAL UNACCOUNTED FOR | | 11.01 | 9.81 | | 1.7 |

Table 2 – Final results

## 4. Conclusions and comments

The application of the described process to the recovery of high-enriched uranium from a UF6 cylinder, and its later enrichment reduction and purification, was successful. 95.1 % of the HEU was recovered and made available for later reuse as LEU.