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Argentina's Efforts to Recover and Down-blend Irradiated HEU from Mo-99 Production Targets

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ABSTRACT

The National Atomic Energy Commission of Argentina has carried out a campaign in order to recover and down-blend its remaining irradiated highly enriched uranium (HEU, from Mo-99 production targets) inventories to low enriched (19,75%±0,2%). The last down-blending batch was completed in march 2016 and the success of this efforts allowed Argentina to be considered HEU free. This irradiated HEU had been stored in two forms, solids on stainless steel filters and solutions. The materials had to be transported from the storage facilities and transferred to the process hot cells where it was purified prior to its down-blending with natural uranium. The hot cell's process involved the dissolution of the solid uranium with nitric acid and its purification by extraction chromatography, using TBP as extractant fixed in an inert support. The final LEU product was converted to an oxide. In the present work technical details of the processing and down-blending processes are describe.

1. Introduction

Under the framework of the Global Thread Reduction Initiative (GTRI), in March 2010, after the RA-6 reactor core conversion, a contract between National Nuclear Security Administration (NNSA-DoE) and the National Atomic Energy Commission (CNEA) was signed in order to eliminate the remaining highly enriched uranium (HEU) inventories not eligible to be returned to the United States because of its form and composition [1]. The works derived from this contract, implied the recovery, purification and down-blending to low enriched uranium (LEU), of all the HEU inventories in Argentina, coming from fresh fuel and target fabrication scraps and irradiated Mo-99 production targets.

All the materials to be processed were classified and divided into six groups. Groups denominated numbers 3 to 5 corresponded to relatively small amounts of fresh materials (liquids and solids) so its recovery, purification and down-blending was carried out without mayor changes in existing facilities before 2015. Inventory from group number 6 (ingots) was, under a special arrangement, down-blended to MEU for U-Mo/Zr miniplates fabrication to be irradiated in the frame of the high density uranium fuels program. In the case of group number 2 (partially hydrolyzed UF_6), several modifications in the Laboratorio Triple Altura (LTA) facility were performed and a special authorization from the nuclear regulatory authorities (Autoridad Regulatoria Nuclear – ARN) was required [2]. The most challenging task, since it corresponded roughly to one half (1.9 kg) of the whole mass that had to be recovered and considering it had been irradiated, was group number 1.

This inventory came from Mo-99 production HEU irradiated targets and had been stored in two forms. Some had been dissolved and stored in the Mo-99 production hot cells as solutions and the rest was still as solids on filters and had been transferred to the waste management area (Área de Gestión Ezeiza - AGE) in the Ezeiza Atomic Center (CAE).

In order to fulfill group 1 task, it was required to refurbish a hot cells radiochemical facility (LFR) at the CAE, which comprised a first step of decontamination of the hot cells and several modifications and maintenance of the facility systems and equipments (hot cells telemanipulators and bootings systems, transfer doors, glove box modification, ventilation maintenance, air-monitoring mounting, etc.). In parallel, the obtention of a new Operations Licence, considering criticality, safeguards, physical protection and facility modifications issues, was required by the ARN, it implied the confection, presentation and approval of the new mandatory documentation and operative procedures. Finally, to operate the facility it was needed to hire and train new personnel; to mount and test process equipment and to design and construct special devices (transport casks, transfer devices, etc.).

The campaign started in 2014 and was finished in March 2016, when the last batch of purified HEU was down-blended. The LEU produced during this operations was sent to the Laboratorio de Uranio Enriquecido (LUE), at the CAE, where it was converted into uranium trioxide.

The project was jointly managed between CNEA and NNSA-DoE. At the Nuclear Security Summit 2016 held in Washington DC, United States of America, Argentina announced the elimination of the remaining inventories of HEU. As consequence of this announcement Argentina (and consequently the whole Latin American and Caribbean Region) is now considered HEU free.

2. Background

Since 1985 Mo-99 is being produced in the Fission Radioisotopes Production Plant, at the CAE. Local Mo-99 demand and part of regional markets are nowadays been supplied by a weekly production of this plant. This production has been carried out irradiating HEU targets from 1985 to 2002 when the targets and production processes were converted to LEU. These operations left the above mentioned irradiated HEU inventories.

The Mo-99 production process starts with a 5 days targets irradiation in the RA-3 reactor, adjacent to the Fission Radioisotopes Production Plant. This targets are then dissolved in a sodium hydroxide solution which dissolves the aluminium cladding and the soluble fission and activation products, among them molybdenum. This solution is then filtered with vacuum through a sintered stainless steel filter. The solution is held to proceed with the molybdenum

radiochemical separation. The precipitate retained on the filter contains the uranium and the insoluble fission and activation products.
The Fission Radioisotopes Production Plant had initially planned to include the recovery of the irradiated uranium, but it was never implemented [3]. The uranium on the older filters was dissolved and stored as solutions in the plant and the rest of the filters were kept in the hot cells to allow them to decay, after several years the filters were packed into cartridges which allowed to accommodate up to four filters each. This cartridges were transferred to the Depósito Central de Materiales Fisionables Especiales Irradiados (DCMFEI), a dry storage facility at the AGE.
Being that this practice has generated difficulties to the radioisotopes production due to the increment in the enrich uranium inventories in the facilities, some options were studied to recover and purify these inventories [4]. These studies were taken as the basis for the process to be implemented in this project.

3. Operations

Firstly, the materials had to be transported from the facilities where they were stored to the LFR. The materials were received and sweep tests for superficial contamination monitoring were performed into both the transport casks and cartridges. Figure 1 shows a cartridge loading operation in the DCMFEI. After that, the materials had to be got into the hot cell. In the case of solutions the transferences were made by a vacuum system. The filters were got into the hot cell through a DPTE® La Calhene system.

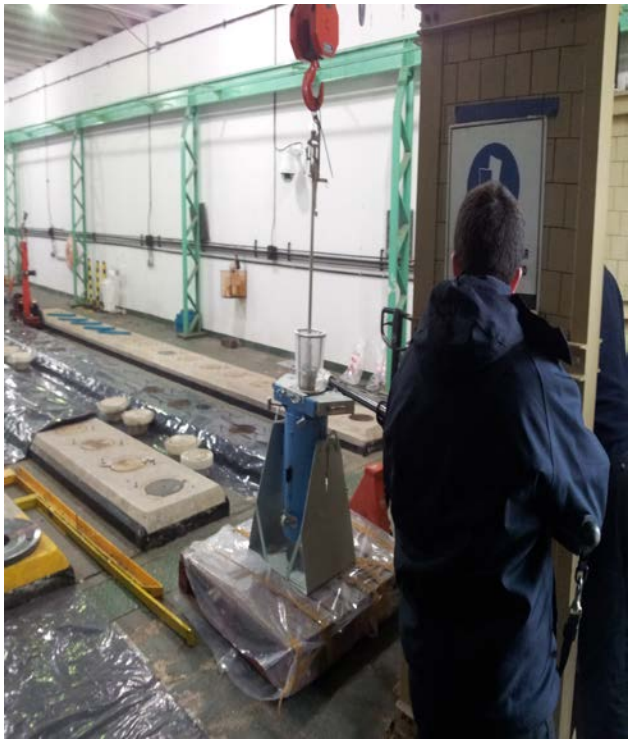

Figure 1 – Cask loading operation at the DCMFEI

The liquids, once inside the hot cell, were analyzed to determine uranium content (Davies-Gray titration method), acidity and enrichment (ICP-MS), adjusted if necessary and purified by an

extraction chromatography process using TBP as extractant, impregnated in XAD-7 support. In the case of the filters, once inside the hot cell, lids were removed, the uranium was dissolved with nitric acid and then filtered, this uranyl nitrate solutions were analyzed, adjusted if needed and purified in the same way. In Figure 2, several pictures of the hot cell operations are shown.

Figure 2 – Top left a filter with its lid, bottom left the dissolver and on the right an overview of the hot cell extraction chromatographic purification process.

After purification, uranyl nitrate solutions were sampled to determine decontamination factors by gamma spectrometry using HPGe detectors and LSC, uranium content (Davies-Gray titration), acidity and enrichment (ICP-MS), transferred by vacuum to the glove box, adjusted and purified again with a similar extraction chromatographic process. In order to optimize time, before every purification process, operational conditions (loading, scrubbing and elution time) were determined using a computational simulation code specifically developed for this process. Figure 3 shows the Operations Room during the process operation. Figure 4 shows a view of the glove box extraction chromatography purification process and the down-blending process. An example of the process simulation code output is shown in Figure 5.

Figure 3 – Operations room overview.

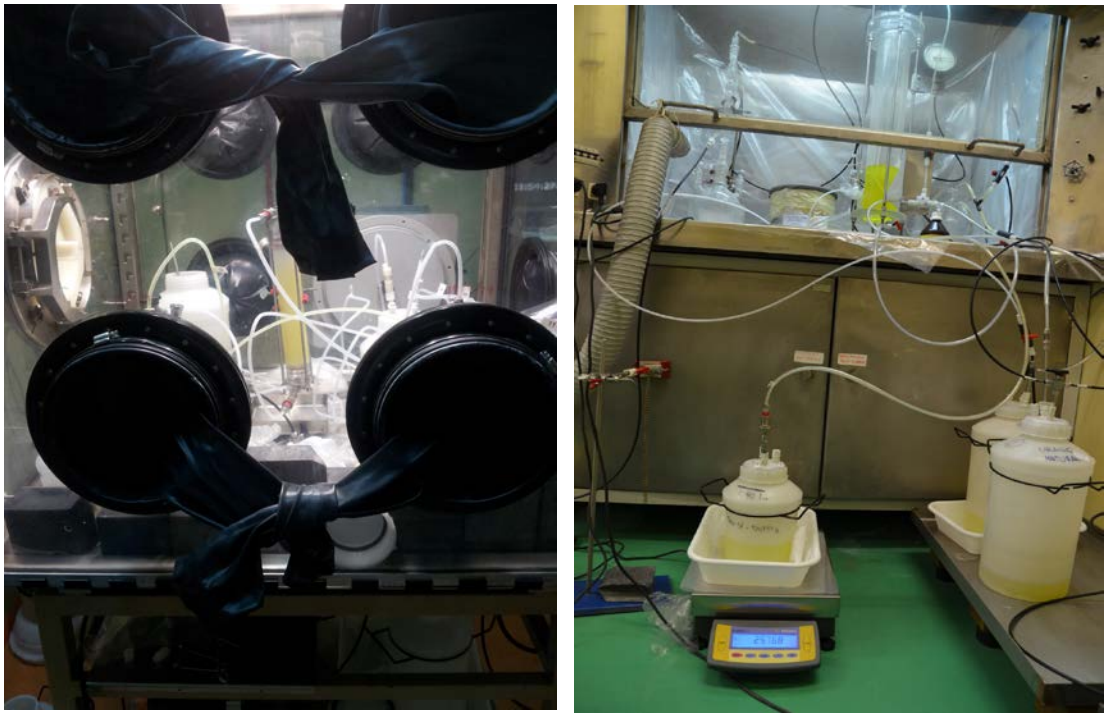

Figure 4 – Glove box process, left and down-blending process, right.

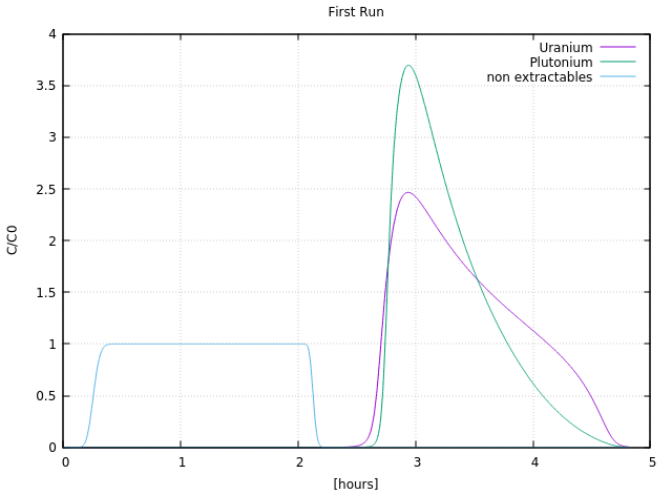

Figure 5 – Process simulation code output.

The final purified HEU product solutions were then sampled to determine uranium content (Davies-Gray titration), isotopic composition (ICP-MS), in order to perform down-blending calculations, chemical (ICP-MS) and radiochemical (alpha spectrometry, gamma spectrometry and LSC) impurities concentration.
These final HEU purified solutions were finally down-blended to LEU by mixing them with nuclear grade natural uranyl nitrate solutions previously obtained by UO_2 powder dissolution.
The mixture was made in a column, the solutions were transferred by vacuum and mixture was agitated with air bubbles.
These LEU solution were sampled again in order to verify U-235 enrichment in the range of 19.75% $\pm$ 0.20%, determine impurities level (ICP-OES).
Finally this solutions were transfered to the LUE facility where they were precipitated as UO_4, filtered, dried and calcined to UO_3. All these operations were carried out inside the LUE facility glove boxes.
The operations needed to complete the recovery, purification and down-blending are schematically described in Figure 6.

Figure 6 – Operations Flow Sheet.

4. Results

Initially, there was neither chemical nor radiochemical characterization analysis of the irradiated materials to be recovered and purified. There were only conservative approximations made using ORIGEN2 code calculations. So the first results to mention is the irradiated material characterization analysis results. Table 1 shows an ICP-MS isotopic analysis composition and Table 2 shows gamma (HPGe 20% relative efficiency detector) and alpha (PIPs detector) spectrometry radiochemical characterization analysis results.

Isotope	%
U-234	0.63
U-235	88.47
U-236	0.64
U-238	10.26

Table 1 - Irradiated HEU ICP-MS isotopic composition analysis (sample 9CC200116).

Radionucleide	Bq/gU
Co-60	3.01E+4
Sr-90	1.30E+5
Sb-125	3.16E+5
Cs-137	2.82E+6
Eu-154	8.20E+4
Eu-155	2.61E+6
Pu-238	1.32E+3
Pu-239/40	1.48E+5

Table 2 – Example of an irradiated (sample 9CC241115 with average 24 years of decay time) HEU radiochemical characterization analysis result.

The chromatographic extraction process had decontamination factor for total beta emitters greater than 10^5. The plutonium was not separated from uranium in this scheme. Table 3 shows an ICP-OES analysis result of a down-blended product.

Element	LEU µg/gU
Al	<5
B	<0.5
Ba	<10
Ca	8.7±0.8
Cd	<0.5
Co	<0.5
Cr	1.6±0.2
Cu	<1
Fe	10±1
K	<20
Li	<5
Mg	2±0.2
Mn	<0.5
Na	<30
Ni	1.0±0.1
V	<0.5

Table 3 – Example of final LEU product ICP-OES impurities analysis (safeguards item U#PD0216).

Regarding recovery yields, the process had a global recovery yield of 91.75%. Anyway, differences were found between historical records (declared amounts) and uranium masses actually found in both, solutions and filters. Differences were attributed to uncertainties of the historical records. Table 4 shows a detail of the HEU accounted masses, Table 5 details the amount of HEU down-blended and finally Table 6 the raffinate solutions uranium content estimation.
Regarding radioactive waste generation, liquid waste (mainly raffinate solutions) have been already managed and solid waste (empty filters, etc.) are still been processed.

Liquids		**Filters**		**Samples**		**Total**	
Total U	U-235	Total U	U-235	Total U	U-235	Total U	U-235
159.31g	141.31g	1031.51g	891.61g	11.90g	10.29g	1202.72g	1043.21g

Table 4 – HEU accounted masses.

Total U	**U-235**
1092.59 g	942.57 g

Table 5 – HEU masses actually down-blended.

Total U	**U-235**
58.58 g	47.18 g

Table 6 – Raffinate solutions uranium content.

5. Conclusion

The campaign was successfully finished, so the aims of the project were accomplished. Argentina (and consequently the whole Latin American and Caribbean Region) is now considered HEU free. Even though according to the lessons learned and the experience gained many aspects might be improved, the

technical feasibility of this process has been demostrated. If this process were regularly operated with LEU irradiated targets (from LEU based Mo-99 production filters) the inventories of this irradiated material would not increase which would have a favorable impact in the LEU based radioisotopes production technology sustainability.

6. References

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