NUCLEAR FUEL CYCLE HEAD-ENDENRICHED URANIUM PURIFICATION AND CONVERSION INTO METAL

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ABSTRACT

The CNEA (Comisión Nacional de Energía Atómica) operates two facilities at the Ezeiza Atomic Center which supply purified enriched uranium employed in the production of nuclear fuels.

At one of those facilities, the Triple Height Laboratory (LTA, Laboratorio Triple Altura), scraps from the production of MTR type fuel elements (mainly out of specification U_3O_8 plates or powder) are purified to nuclear grade. The purification is accomplished by a solvent extraction process.

The other facility, the Enriched Uranium Laboratory (LUE, Laboratorio de Uranio Enriquecido) produces 90% enriched uranium metal to be used in Mo 99 production (originally, the uranium was used for the manufacture of MTR fuel elements made of aluminum-uranium alloy). This laboratory also provided metallic uranium with a lower enrichment (20%) for a first uranium-silicon testing fuel element, and in the near future it is going to recommence 20% enriched uranium related activities in order to provide the metal for silicon-based fuel elements production (according to the policy of enrichment reduction for MTR reactors).

INTRODUCTION

The Argentinean National Atomic Energy Commission (CNEA) operates two nuclear facilities, the Enriched Uranium Laboratory (LUE) and the Triple Height Laboratory (LTA) (both located at CAE, the Ezeiza Atomic Center), that play a significant role in the production of irradiation targets by providing nuclear material for the production of fission Mo-99 and MTR fuel elements.

At these two facilities (LUE and LTA) the recovery of nuclear material (enriched uranium) contained in scrap of different types is accomplished by the use of selective chemical processes and a highly purified material (suitable for nuclear applications) is obtained. Additionally, conversion into metallic uranium is carried out in the LUE.

These two laboratories might contribute to the LEU project by providing metallic uranium for the following purposes:

- Manufacture of fuel elements based on U_3O_8 for the RA-3, an MTR reactor located at the CAE.
- The program for the development of MTR type fuel elements employing silicon-uranium alloys.
- Manufacture of irradiation targets for the production of fission Mo-99.

Moreover, the recovery of scrap generated at the different stages of the manufacture of fuel elements permits a reduction in the non-operative inventory and enhancements in the safeguards for the existing nuclear material in the LEU fuel cycle.

The LUE and LTA facilities are not authorized to process irradiated material. Besides, they don't meet the technical and security conditions required for that purpose.

The goal of this paper is to transmit the main features and operating experience obtained from these two facilities, in the hope that they can be useful in the LEU project.

TRIPLE HEIGHT LABORATORY (LTA)

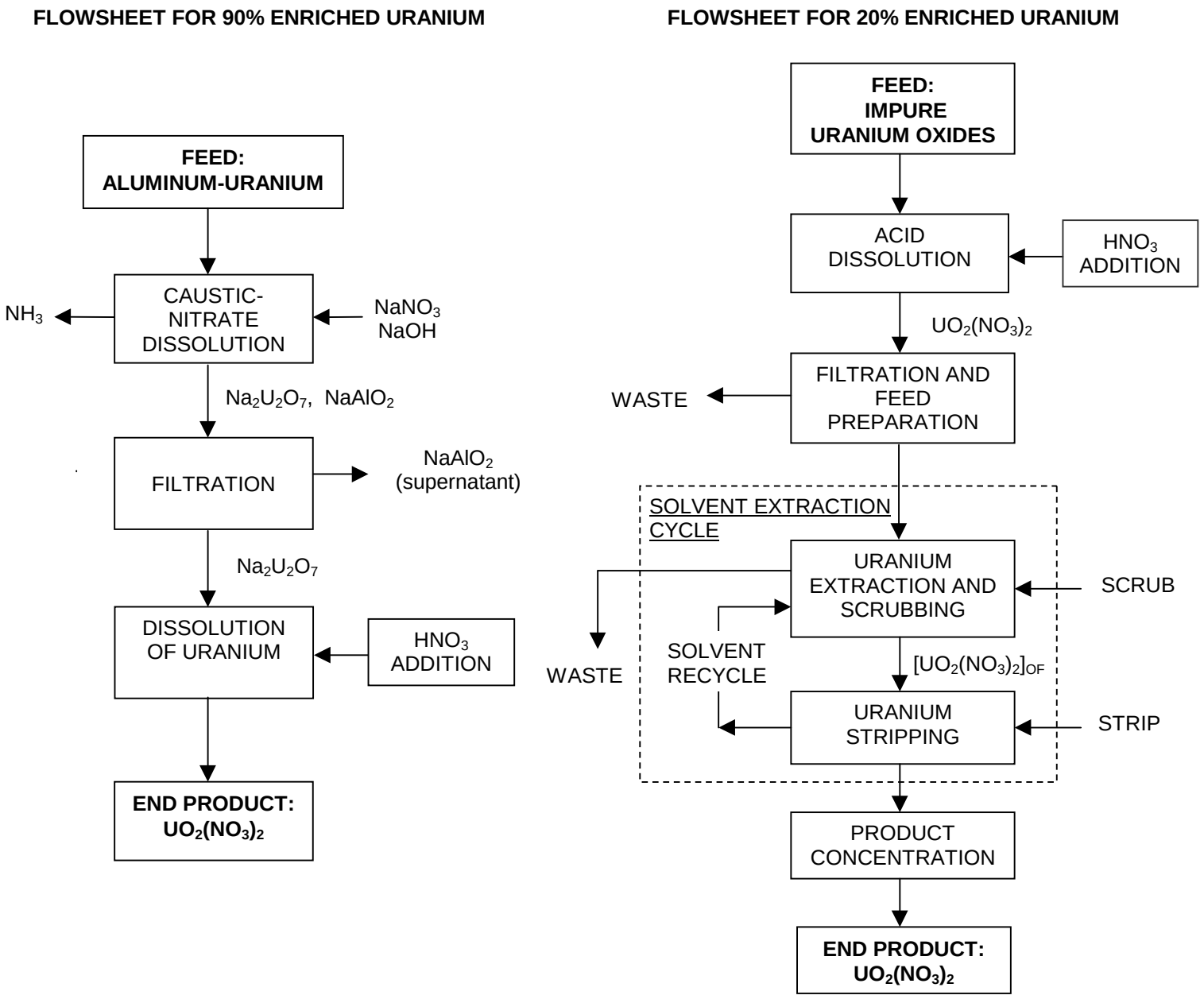
Recovery processes involving 20% and 90% enriched uranium are carried out in this facility (see Fig. 1).

Recovery of 20% enriched uranium. The nuclear material present in scrap from the manufacture of fuel elements -both U_3O_8 powder and Al/U alloy- is recovered. The process stages are:

a) Dissolution of the material from which the uranium is to be recovered.
b) Filtration and preparation of the feed solution.
c) Purification by solvent extraction.
d) Concentration of the final uranium solution

a) Dissolution: HNO_3 is employed in order to obtain uranyl nitrate solution. Aluminum-uranium alloys are dissolved using $Hg(NO_3)_2$ as a catalyzer. An alkaline dissolution in the presence of nitrates -to separate the aluminum- is also used, followed by a dissolution of the uranium compound with nitric acid.

Figure 1. LTA Laboratory Flow Diagram for Uranium Recovery



b) Filtration and adjustment: Silica and other insoluble materials present in the acid solution are separated. Afterwards, concentration and acidity are adjusted for the solvent extraction stage.

c) Purification by solvent extraction: The uranyl nitrate solution is purified -using a mixture of dodecane and tributyl phosphate (TBP) as a selective solvent- in a single extraction cycle. The final product is a uranyl nitrate solution of high purity from which U_3O_8 powder destined to the manufacture of fuel elements can be obtained.

d) Concentration of the final uranium solution: If necessary, the final product is concentrated in a rotary evaporator.

Recovery of 90% enriched uranium. Presently, and until the plant that produces fission Mo-99 is capable of working with lower enrichments, the 90% enriched uranium present in stored scrap from the manufacture of Al/U fuel elements needs to be recovered. In this case the aluminum is separated from the uranium and the latter is transferred -as a uranyl nitrate solution- to LUE to be converted into metal.

The process stages are:

a) Alkaline dissolution in the presence of nitrates.
b) Separation from the sodium aluminate solution by filtration.
c) Dissolution with nitric acid.

a) Alkaline dissolution: $NaNO_3$ and NaOH solutions are employed to obtain a sodium diuranate solid and separate the aluminum as sodium aluminate in the liquid. Under these conditions, the H_2 concentration is reduced, and therefore the risk of explosion in the off-gas is lowered. An excess of NaOH is used to ensure the stability of the aluminate solution. The presence of carbonates is controlled to minimize the uranium losses in the liquid.

b) Separation of the sodium aluminate: the liquid is separated from the insoluble uranium compound by sedimentation and filtration. The solid is then washed with a NaOH solution to eliminate most of the aluminum. Finally, deionized water is employed to reduce the alkalinity of the solution that impregnates the solid.

c) Dissolution with nitric acid: A solution of uranyl nitrate, practically free of aluminum, is obtained.

Equipment. A 50 liter, stainless steel vessel (with reflux condenser and gas scrubbing column) is employed for the dissolution. The material to be dissolved is put directly into the vessel from the inside of a glove box.

Filtration is done under vacuum. The filtering medium is a stainless steel “felt” with a diameter of 14 cm. Diatomaceous earth is used as a filtering aid. The solvent extraction process is accomplished in two mixer-settler batteries, each one having 12 stages. Those batteries are not employed with 90% enriched uranium.

A 10 liter rotary glass evaporator is used to concentrate solutions.

Chemical control. Measurements of the amount of uranium in the input and output streams are done for purposes of account of nuclear material. All uranium determinations are done in an Analytical Laboratory associated to the LUE and LTA facilities. The analytical laboratory is presently participating in a qualification program sponsored by ABACC. It also took part in intercomparison essays with France and the DOE. The results obtained so far are satisfactory.

ENRICHED URANIUM LABORATORY (LUE)

Processes of purification and conversion into metal are performed in this laboratory. The main stages are (see Fig. 2):

a) Preparation of the feed: Depending on the material to be processed, different operations may be necessary: a dissolution with nitric acid in the case of powder, or concentration if a very diluted uranyl nitrate solution is received.

b) Uranium peroxide precipitation: this highly selective reaction, which permits the denitration of the uranium solution and the elimination of many impurities, is suitable for the production scale of the laboratory. During the reaction, pH is controlled by the addition of concentrated ammonium hydroxide solution. The destruction of the hydrogen peroxide by the iron present in the solution is avoided by adding citric acid and malonic acid to it. If the uranium losses in the filtrate are too high, the uranium is recovered using a small column filled with TBP/Kel-F.

b) Calcination to UO_3: It is done under air, at a temperature of 260 C. If the material is very impure, the UO_3 is recycled for a second precipitation.

c) Calcination to U_3O_8: An argon atmosphere is employed. The material is heated at 800 C for 8 hours. The obtained U_3O_8 is sampled and analyzed to measure the amount of uranium in the batch.

d) Reduction to uranium dioxide and hydrofluorination: Reduction is done with a H_2-N_2 mixture at a temperature of 600 C. Afterwards, temperature is reduced to 450 C and a mixture of HF, H_2 and N_2 is fed to transform the UO_2 into UF_4.

e) Metal reduction: UF_4 and calcium are mixed and loaded in a magnesium oxide crucible, which is put inside a steel reactor. The reactor is purged with argon and hermetically sealed. The calcium thermite reaction is obtained by heating in an induction furnace. Once cooled, the reactor is transferred to a glove box and opened in an argon atmosphere, and the metal is separated from the slag and the remains of the crucible.

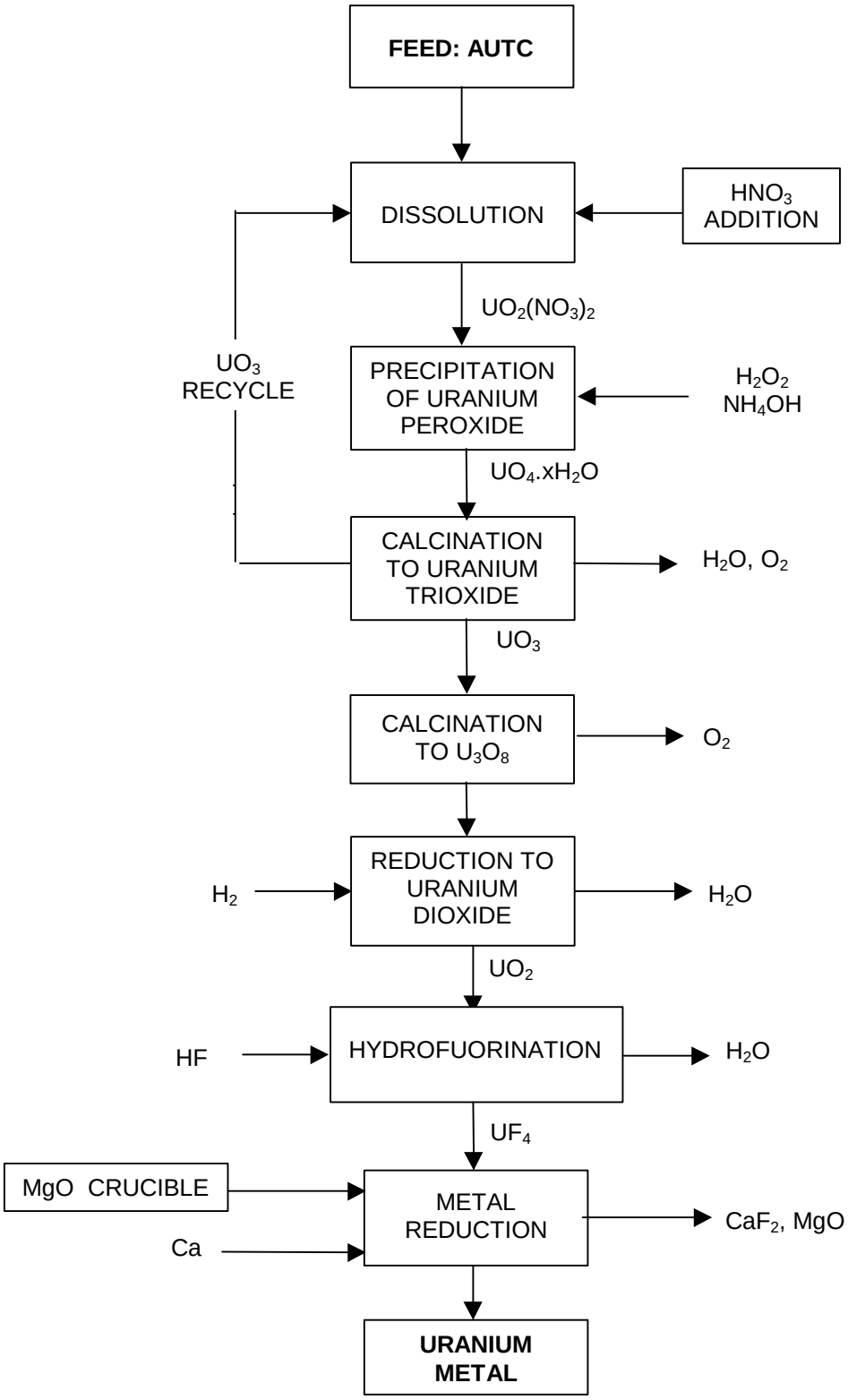


Figure 2. LUE Laboratory. Flow Diagram For Uranium Metal Production.

Chemical control. Samples for uranium analysis are taken for nuclear material account purposes at three points in the process: after dissolution or concentration of the material received by the laboratory, in the solution left after the precipitation, and after calcination to U_3O_8. Another control point is the weighing of the metallic "button". Impurities are analyzed in the U_3O_8 sample. The analysis are performed in CNEA's centralized laboratories A typical analysis is shown in Table 1.

Uranium 235, wt. %	89.94
Boron, µg/g	~ 1
Cadmium, µg/g	< 0.5 D
Silicon, µg/g	<20 D
Iron, µg/g	<20 D
Magnesium, µg/g	< 5 D
Manganese, µg/g	< 3 D
Nickel, µg/g	< 6 D
Aluminum, µg/g	~10
Vanadium, µg/g	~ 5
Cooper, µg/g	< 3 D
Cobalt, µg/g	< 3 D
Calcium, µg/g	<10 D
Chromium, µg/g	<15 D

D: Detected

Table 1. Typical Analysis Of U_3O_8 (90% Enrichment)

Equipment. LUE can be defined as a small auto-integrated radiological facility. It contains 4 glove boxes and a radiochemical hood located in a ventilated area. The boxes are grouped in two lines:

a) Wet line: 2 boxes for dissolution, precipitation and calcination to UO_3. Each batch has 250 g of total uranium.

b) Dry line: 2 boxes for calcination to U_3O_8, reduction to UO_2, hydrofluorination, and loading and unloading of the metal reduction reactor. In the metal reduction stage each batch has 500 g of total uranium. In the rest of the dry line the batches are 250 g each.

The main process equipment includes:

- Dissolution and uranium peroxide precipitation: standard laboratory glass equipment with a total volume of up to 2 liters.
- Filtration of uranium peroxide precipitate: Stainless steel filter with sinterized plate. Porosity: 5 µm.
- Calcination to uranium trioxide: A vertically mounted cylindrical furnace is used. A glass beaker of 1000 ml capacity put inside the furnace contains the uranium peroxide.

- Calcination to U_3O_8: Uranium trioxide is calcinated in a platinum crucible inside a vertical furnace.
- Reduction to uranium dioxide and hydrofluorination: It is done in a horizontal furnace made of Hastelloy. The material is in a tray made of Hastelloy and lined with platinum.
- Reduction to metallic uranium: A stainless steel pressure reactor with a bolted cover plate and a magnesium oxide crucible are used. The material is heated by a 50 kW induction furnace.

LICENSING REQUIREMENTS AND SAFEGUARDS

Both facilities are authorized to process non irradiated material, by the International Atomic Energy Agency (IAEA), by the Brazilian-Argentinean Agency for Account and Control of Nuclear Materials (ABACC) and by the Argentinean Nuclear Regulatory Authority (ARN).

Each of these two laboratories is a nuclear material balance area and fulfills the following safeguard requisites:

- The application of the Account and Control Common System (SCCC) demanded by ABACC, for the fulfillment of the quadrilateral agreement between Argentina, Brazil, ABACC and OIEA (INFCIRC 435).
- To perform chemical controls for the determination of the mass of material processed by the facilities and for the information about the material flow between balance areas.
- To carry out the annual physical inventory determination.
- To receive the accounting and physical inventory audits performed jointly by ABACC and IAEA.
- To notify any modification in the process beforehand.
- To notify changes in the enrichment of the material to be processed.
- To have account registers differentiated by source of the material to fulfill the requirements of the agreement with the USA (INFCIRC 130).
- To notify about changes in the chemical or physical form of the material (U 90%) from the United States, authorized for its use in the production of Mo-99.

RADIOLOGICAL SAFETY

In these laboratories the radiological risks are associated with the radiological properties of enriched uranium, due almost entirely to alpha particles, principally from the U-234 isotope of uranium. Gamma and beta radiation effects are practically negligible.

LUE and LTA have received their operation licenses, granted by the ARN, for the processes previously mentioned. These documents fix the maximum mass allowed in each laboratory, depending on the enrichment and the process, in order to prevent nuclear accidents. Safety margins are taken to ensure that under any circumstances the process will be far from a critical situation. The documents also establish that the operation of both facilities is ruled by procedures written in practice codes, security manuals, operation manuals, occupational controls, environmental controls, etc.

The operating staff is licensed for each function and their specific authorization must be periodically renewed. The laboratories operate with only one degree of enrichment each time. The amounts of uranium or uranium compounds incorporated by the operating personnel have given no cause for concern and radiation exposures were kept at very low levels.

OPERATING CAPACITY

LTA. It began to operate in 1994 and has processed a total of 7040 g of 20% enriched uranium. Presently work is in progress for the recovery of 90% enriched uranium contained within Al/U plates. The uranium recovered is transferred to LUE in order to proceed to its transformation into metal.

Operating capacity of LTA (one working shift per day):

a) Process for the recovery of 20% enriched uranium:
   Batches of up to 2000 g of total uranium. Production capacity: 6 kg/yr.

b) Process for the recovery of 90% enriched uranium:
   Batches of up to 80 g of total uranium and 2000 g of aluminum maximum.

LUE. Form the beginning of the operations in 1981 this laboratory has processed 19 batches of 20% and 90% enriched uranium. The reduction to metallic uranium stage based on the calcium thermite reaction has performed extremely reliably. Yields varied between 93% and 98%, with the losses mainly in the slag from the metal reduction. No recovery treatment is attempted for the uranium contained in the slag.

Presently, ~ 475 g metallic buttons of 90% enriched uranium are being produced to be used in the manufacture of irradiation targets for the production of Mo-99.

Production capacity of the LUE (one working shift per day): 5 batches/yr., with approx. 475 g of total uranium each. (for a processed mass of uranium of 500 g).

Plans for the future.

LUE. In the medium term the scale of this laboratory will be enlarged to handle batches of approximately 2000 g of 20% enriched uranium. The increased amounts of metal are required for the manufacture of silicon-uranium MTR fuel elements, within the frame of the new program for the development of high density fuel elements.

LTA. This laboratory is often modified to treat new materials. At present time the facility is being prepared for the recovery of 90% enriched uranium from a clogged UF_6 cylinder containing partially or totally hydrolyzed material as a consequence of an accidental water entrance during the manufacture of aluminum-uranium alloy.