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Development of a Process for the Purification of Mo-99 Obtained by Irradiation of Uranium Solutions

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ABSTRACT

During the period 2008-2011, INVAP developed a process for the production of Mo-99 from a low enrichment uranyl nitrate solution, similar to those that would be obtained from a solution nuclear reactor.

The work was performed for B&W and included different and sequential phases of increasing complexity and radioactive inventory. It encompassed the theoretical study of the operational conditions for the separation process, definition of the working plan and the experimental separation and purification of Mo-99 in representative scaled down experiments.

The results of this experimental program can be summarized as: obtainment of information from the irradiation of solutions, search/design/testing of adsorbents and separation stage, and demonstration of the purification process.

The entire process has demonstrated the feasibility of producing high activity, high purity, Mo-99 as a precursor for Tc-99m, meeting the required pharmaceutical specification.

1. Introduction

Mo-99 is widely used in nuclear medicine. It produces the short half-life and low energy daughter nuclide Tc-99m.

Numerous methods for the separation and purification of Molybdenum from fission products had been reported, as the processing with different alternative steps of irradiated uranium targets and the separation from a solution nuclear reactor (in this particular case uranyl nitrate solution).

Up to the presented program, only few process related to the first philosophy are used commercially, and the process for the separation and purification from solution nuclear reactor was not developed, and reported experiments were promising but, uncompleted and not fully representative of the real situation.

The principal conceptual differences of the existing commercial used processes with this separation process are the constraints related with the reutilization of the reactor fuel: higher radiation doses during the separation (originated in the multiple irradiations, higher uranium inventories and processing times) and the necessity of separation materials and process that do not contaminate the solution.

The suggested method for the molybdenum separation from a solution of a solution nuclear reactor is based on the contact of the solution (fuel of the reactor) with a material which selectively adsorbs or reacts (reversibly) with the Mo-99, and do not adsorb or react with the rest of the nuclides and uranium.

The success of this process depends on the specific interaction of each nuclide with the sorbent, a phenomenon defined by the characteristics of the environment (solution and radiation), the chemical characteristics of the sorbent and the operational conditions. And once the Mo-99 is separated from the uranyl nitrate solution, a special chemical process must be used in order to purify and reach a high purity Mo-99

INVAP defined an integral program that minimized the risks associated to any research & development effort and employed in the most efficient way the resources so far available – both technically and economically. Including different and sequential phases of increasing complexity and radioactive inventory. It encompassed the theoretical study of the operational conditions for the separation process, definition of the working plan and the experimental separation and purification of Mo-99 in representative scaled down experiments.

The outlines of the research and development program, which demonstrated the viability of utilizing a solution reactor to produce Mo-99 can be summarized by the following tasks:

- Sorbents Characterization and Selection.
- Mo-99 Separation Experimental Tests with Non-Irradiated Material.
- Mo-99 Separation and Purification tests with irradiated material from a LINAC.
- Mo-99 Separation and Purification tests with irradiated material from a Mini Loop.

2. Sorbents Characterization and Selection

Hundred and four existing reports and articles and non-published resources on potential sorbents for Mo-99 separation from an uranyl nitrate solution were studied, in order to categorize their known sorption characteristics and defined their success viability for the proposed use.

The study defined boundary conditions and provided a detailed review of the behavior of the different sorbents candidates in the process.

For the reactor solution to be processed, the mean items under consideration were:

- Concentration of nuclides.
- Concentration of uranium and nitrate.
- Concentration of nitric acid.
- Corrosion products.
- Temperature.
- Radiation doses.

For sorbent selection and testing, the mean items under consideration were:

- Selectivity.
- Kinetics.
- Molybdenum stripping capability.
- Radiation doses resistance in the range of 10 to 100 MRad.
- Low reactivity with nitric acid (low solubility).
- Particle size and distribution.

In relation to the separation system design, the mean items under consideration were:

- Addition of oxidants.
- Fluid dynamic considerations.
- Processing time.
- Temperature.

Finally as a conclusion to this work, eight candidates were identified as potentially good candidates for Mo-99 separation from uranyl nitrate solutions. Five of them were new ones in the sense they were never proposed for this use. The physic and chemical behavior of the candidates was established, which, together with the summary of the influences of the different variables, allowed to define the complete working plan.

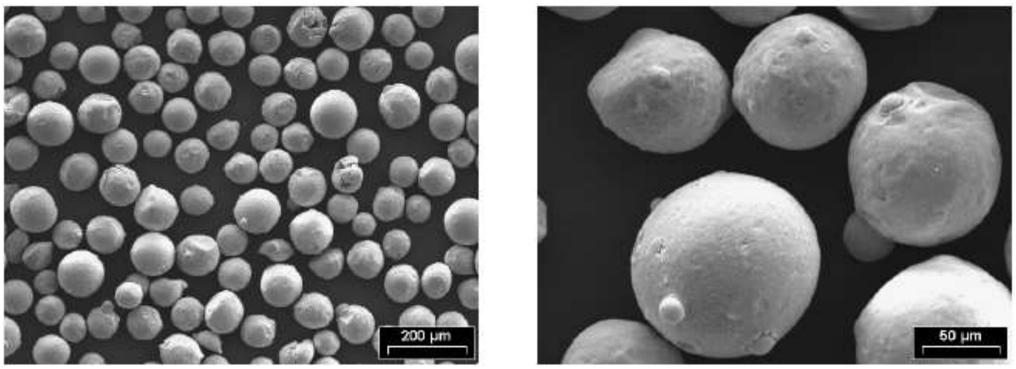
3. Mo-99 Separation Experimental Tests with Non-Irradiated Material

During this experimental task, the candidates from the previous work were tested and ranked according to their properties and capabilities in the Mo-99 separation.

Simple tests with non radioactive material and radiotracer were used during this phase of the development plan. Very low radioactive inventories allowed a high quantity of tests and the study of variable effects with a lower effort.

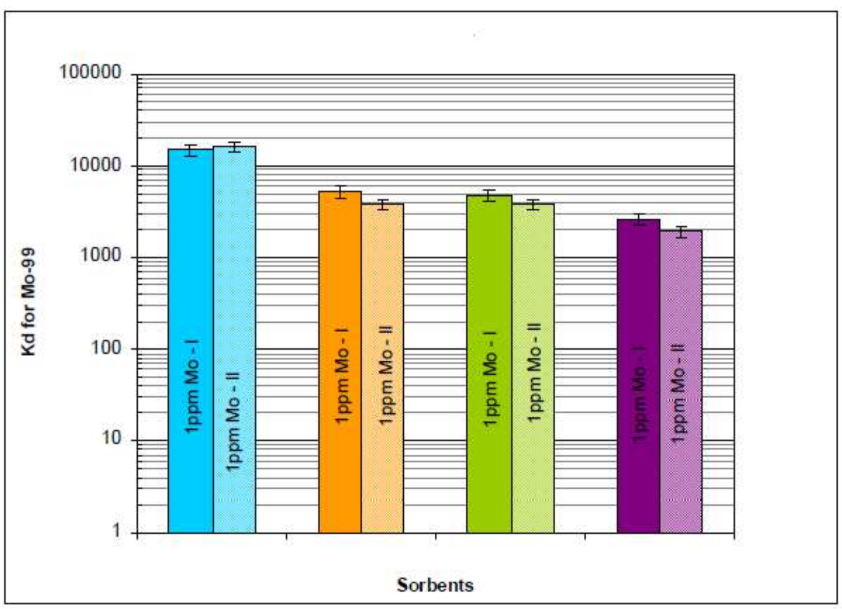
The work was divided in consecutive stages. Each one with acceptance criteria which defined materials and conditions to be tested in the next stage.

Initially, physical-chemical characterizations of wet and dry sorbents were determined, selecting those materials which demonstrated good physic-chemical resistance to chemical solutions and better fluid-dynamic behavior when is loaded in the chromatographic column.



Photos obtained with SEM for a specific sorbent

After, sorbents were categorized and selected according to their batch selectivity to Mo-99, testing the influence of pH, uranium concentration and temperature. Those materials that had shown a low selectivity were rejected



Batch Selectivity (duplicated tests)

Finally, the selected sorbents were tested using them in chromatography separation columns, studying the influences of the different variables on molybdenum's yield and uranium's losses.

As a result of the laboratory work, materials were selected and a small scale separation process was defined.

4. **Mo-99 Separation and Purification tests with irradiated material from a LINAC**.

This stage included the laboratory testing of selected sorbents under irradiation. Encompassed a series of tests in which the effects of radiation) on the separation process was assessed.

The irradiation source was the main beam of 25MeV of the Linear Electrons Accelerator (LINAC) which is a facility of CNEA, located in Bariloche Atomic Centre (Centro Atómico Bariloche).

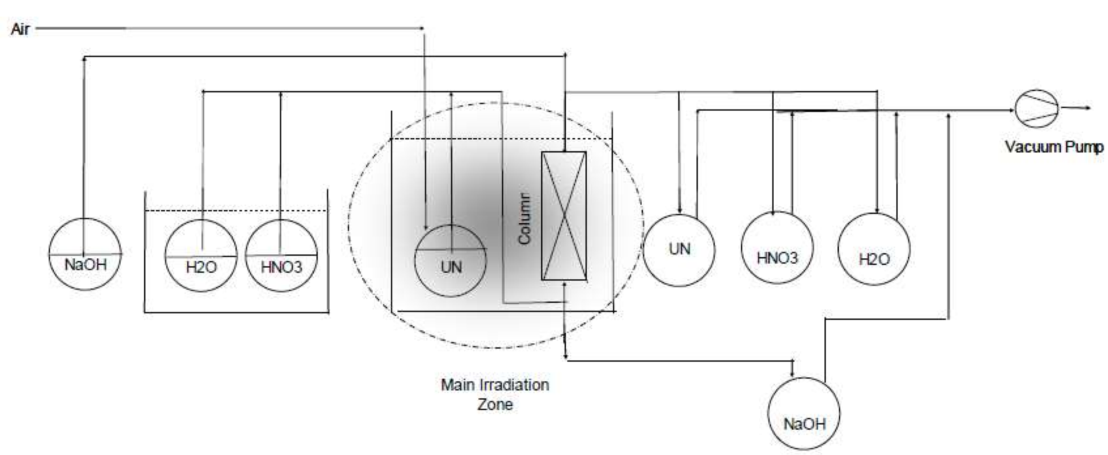
Main beam was used, irradiating an Aluminum Cooled Target in order to have a gamma radiation fields. The gamma energy was used for the study of effect of radiation on the sorbents and for the small production of fission products by photo-fissions on U-238.

Dose rate characterization and photo-fissions yields measurement were done in order to define the experimental program. Those components located nearest the Aluminum target were under a gamma dose greater than 4 Mrad/h.

Isolated sorbents, and sorbents in water and in acidic media were irradiated in order to assess the effect of radiation and radiolysis products, on its properties. These irradiated sorbents were tested in batch and in column mode, following the steps previously described in order to determine, by comparison, the impact of radiation and operative conditions on its properties/behaviour.

After, an uranyl nitrate solution as well as the sorbents in a column were irradiated locating the set-up in front of the gamma-beam, then the molybdenum and others fission products separation was tested, also under irradiation. The irradiation was such that the achieved accumulated dose along the experiment was representative of the real case.

Following the scheme of the system designed for tests under irradiation.



Scheme of the system

Photographs of the system

All the system was controlled remotely, from outside the LINAC's bunker. The design and its remotely control employment were not only important for the tests under irradiation but also for its future application in hot cell work.

On each test, a sample of the UN solution after the irradiation and before column loading was taken, as well as a sample of the UN solution just before its passage through the column. Sample of washings and elution solutions were also taken. All samples were measured and analyzed in order to evaluate behavior of Mo-99 and relevant nuclides along separation for the different materials under test.

The results found along the tests were in accordance with the findings expected and reported on the previous stages of this program. The selection of possible sorbents, their behavior under several variables as well as the identification of possible Mo contaminants are some of the most relevant examples.

5. Mo-99 Separation and Purification tests with irradiated material from a Mini Loop.

The tests had as objective to determine the behavior of the separation and purification process in an environment of radionuclide diversity with high activity concentration.

Testing in this stage was fully representative (in small scale) of all the conditions reached in the full scale system. For this propose a mini loop was designed, installed and operated, where all the conditions in the solution nuclear reactor were replicated.

In order to define the framework for the operative conditions and on the basis of the results from previous stages, the following issues were evaluated before and after the runs:

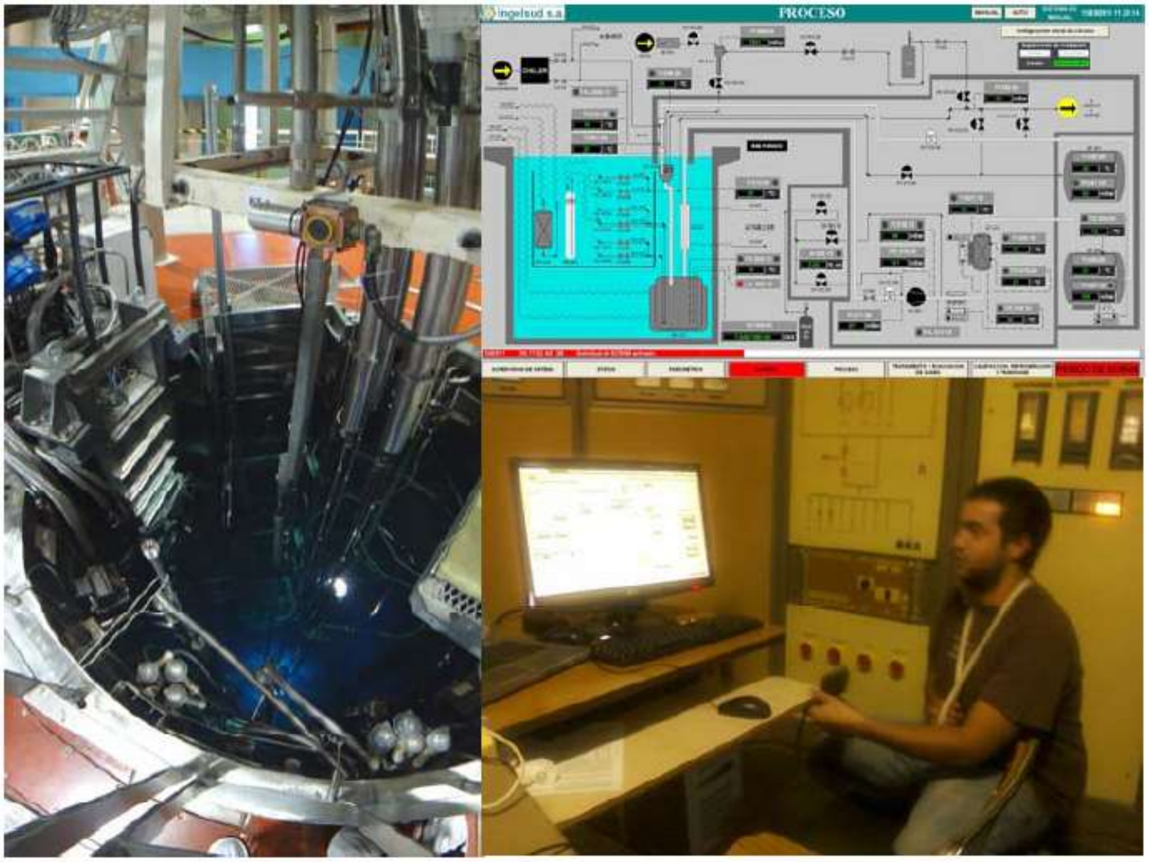
- The operative conditions during the Mo-99 generation process: neutron flux, power density, radiolysis induced gas production, chemical and radiochemical composition, and non-soluble chemical compounds.
- The operative conditions during the separation process: chemical species and specific activity.

During the testing of the separation and purification process, the following activities were performed:

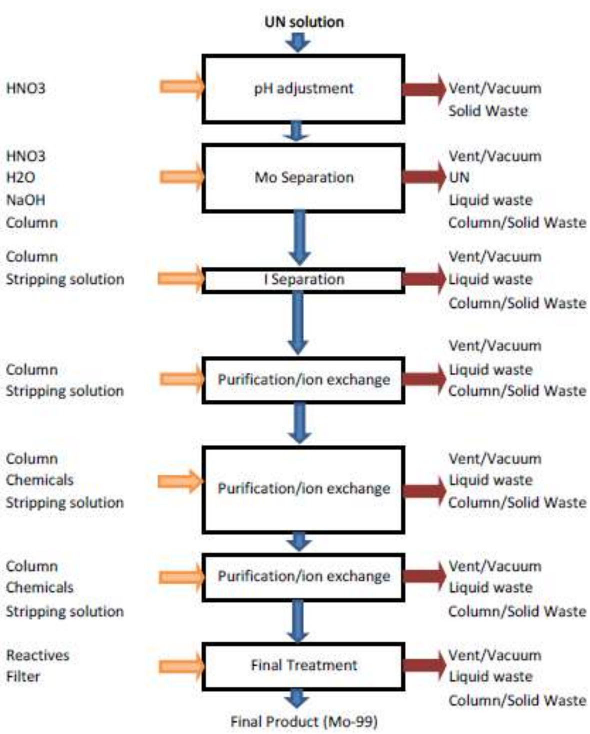
- Preparation of the solution
- Irradiation
- Transport of solution
- Hot cell work: Adjustment of solution, Mo-99 separation and Purification
- Waste management
- QC of product
- Characterization of streams

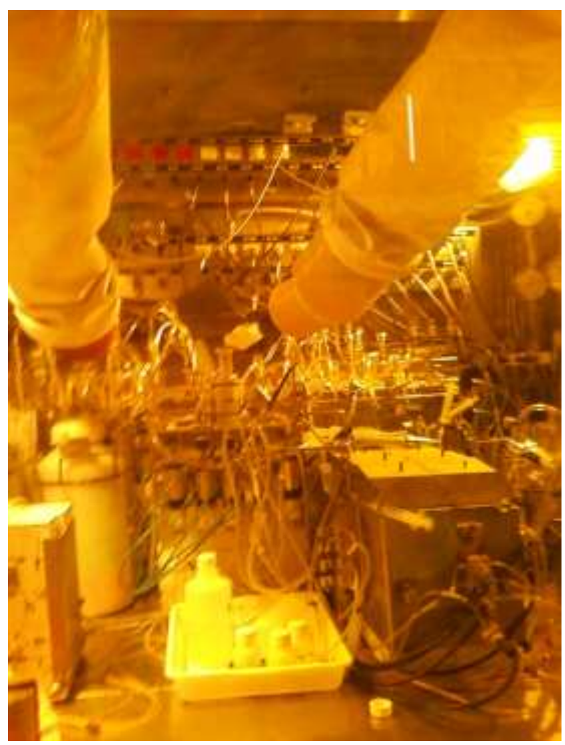
In order to perform the work the following dedicated equipment was specially designed and constructed in the RA6 Reactor (located in the Bariloche Atomic Center):

- Irradiation loop
- Hot cell
- Automatic separation and purification processing system
- Transfer shielding
- Glove box
- QC laboratory



Photographs of the systems





Process Flow Diagram – Process Equipment in hot cell

The results of these experiments were:

- Mini-Loop design and operation parameters.
- Determination of the effect of radiation on separation of molybdenum and other radioisotopes.
- Determination of Mo-99 separation factors.
- Determination of the effects/interference/competition of irradiation fission products on product uptake, fixation and retention of Mo-99.
- Quantification of separation process efficiency and uranium hold-up.
- Quantification of column sizing/flow rates for optimal, efficient separation.
- Contamination of the fuel including sorbent dragging during the separation process.
- Elution yields and flow rate/conditions.
- Conduct demonstration trials and verify analytical techniques.
- Confirmation of stages for the purification process.
- Quantification of contaminants in the different streams.

The entire process has demonstrated the feasible production of high specific activity, pharmaceutically acceptable Mo-99, as a precursor for Tc-99m from an irradiated low enrichment uranyl nitrate solution fuel.