Laboratory Research on Back End Issues of the Mo-99 Production

Falcon, M. : Russo, A. ; Schickendantz, F. ; Vaccaro, J.
Unidad de Actividad Materiales y Combustibles Nucleares - CAE – CNEA
e-mail: falcon@cae.cnea.gov.ar, russo@cae.cnea.gov.ar, schicken@cae.cnea.gov.ar,
vaccaro@cae.cnea.gov.ar

Introduction

The Argentinean National Atomic Energy Commission (CNEA) is now beginning to produce fission ^{99}Mo (parent of the radionuclide ^{99m}Tc, widely used in medicine) by irradiation of targets containing 20% enriched uranium. The reduction from the previously employed enrichment of 90% implies an increase in the mass of uranium necessary to produce the same ^{99}Mo activity. This, and the fact that the irradiated uranium has a very low burn-up, led to the decision of studying the feasibility of a method for the recovery (and later reuse) of the irradiated uranium, in order to reduce purchase and post-irradiation storage costs. This task is part of a project for to improving several aspects of the ^{99}Mo production process (including the recovery and purification of other valuable fission products, such as ^{137}Cs, ^{90}Sr and ^{133}Xe).

The process for ^{99}Mo purification begins with the dissolution of the target. Currently, an alkaline dissolution process is used, from which a solution containing ^{99}Mo and other fission products (e.g. ^{137}Cs) is obtained. The uranium (and with it several fission products) is not dissolved and must be subjected to an acid attack prior to its purification. In other processes presently under study, the target is entirely dissolved and the uranium accompanies the molybdenum through the first part of the (Mo) purification process. In any case, the input to the (U) purification process would be a solution of irradiated uranium, contaminated with fission products and actinides.

This research is focused on the separation of beta/gamma emitters from the uranium, a process that has to be conducted in shielded cells with alpha confinement. The eventual need for additional purification from alpha emitters has not yet been established, but such a process would be -in principle- simpler to implement, because only alpha containment (glove boxes) would be necessary.

To estimate the required decontamination factor (DF) for the uranium recovery operation, the irradiation of the target was simulated with the Origen 2 (8) computer code. It was assumed that no partition of the fission products occurs during the dissolution (the less favorable case). The activities of the fission products (FP) were calculated for different cooling times. These activities were in turn converted to gamma dose rates (using the energies and yields of the main gamma lines of each FP). Finally, the required DFs (in terms of total gamma dose rate) were obtained by estimating an acceptable dose rate for later stages of the recovery process (to be done in glove boxes).

Figure 1 shows the contribution of the principal gamma emitters to the dose asociated to the irradiated uranium, after a cooling period of nine months. The ^{95}Zr-^{95}Nb pair is the most important contributor, with about 90 % of the total dose rate, followed by other FP such as ^{103}Ru and ^{137}Cs, which are of less importance. The long-lived radionuclide ^{137}Cs becomes the most important contributor only after two years of cooling.

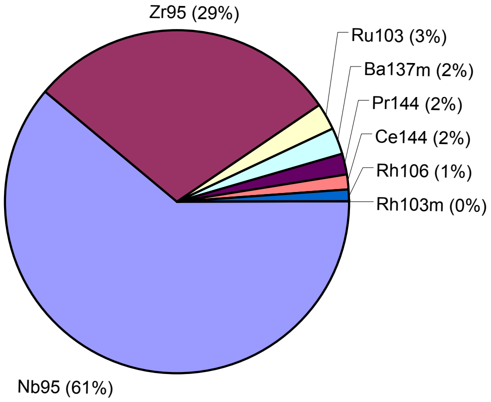

Figure 1: Gamma dose composition after 9 months of cooling. Total dose rate: 218 mGy/h per gram of U 20%. 5 Days Irradiation

Figure 2 is a plot of the required DF (in terms of the total dose rate) versus the cooling time. The lower curve corresponds to a material from which the ^{95}Zr-^{95}Nb pair has been eliminated. It can be seen that for cooling times shorter than two years this elimination reduces several times the required DF (i.e. the dose rate). Even for longer times these isotopes are second in importance, after cesium. Moreover, both nuclides are not easy to eliminate by the selected uranium purification methods (see below). From these observations it was concluded that it is worthwhile to study specific methods to eliminate these two isotopes, in addition to general techniques for uranium purification.

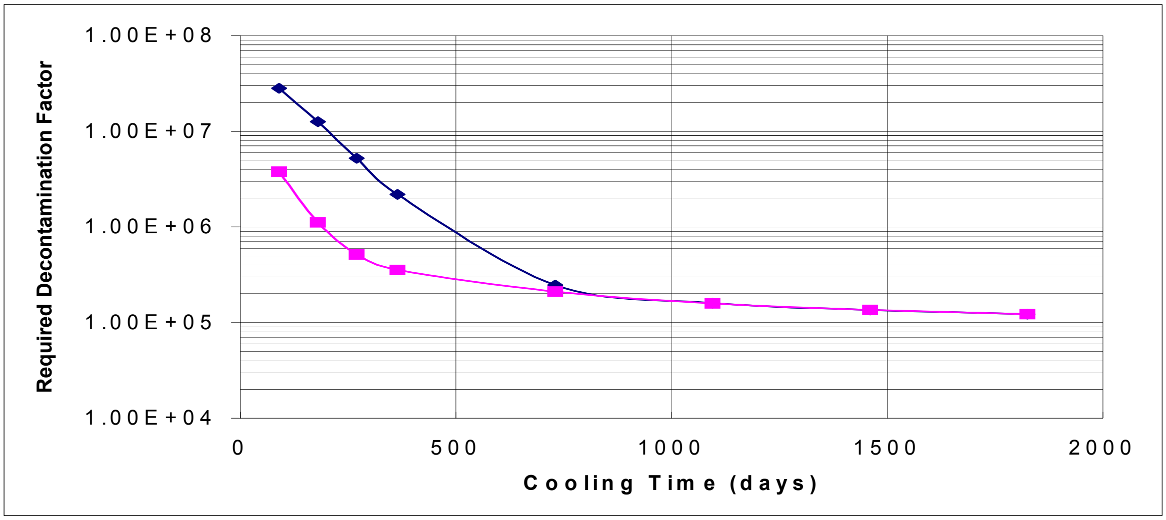

Figure 2: required decontamination factor (in terms of dose rate) as a function of time.

The optimal cooling time would reflect a tradeoff between the convenience of a reduced uranium inventory and the dificulty of attaining high decontamination factors. One of the objectives of the present task is to acquire the necessary information for that estimation.

Based on bibliographic data (1) a preliminary flowsheet (Figure 3) was proposed as a guide for the development work. It consisted of two uranium purification stages (a ion exchange and chromatographic extraction), with a Zr-Nb separation step based on adsorption in silica gel.

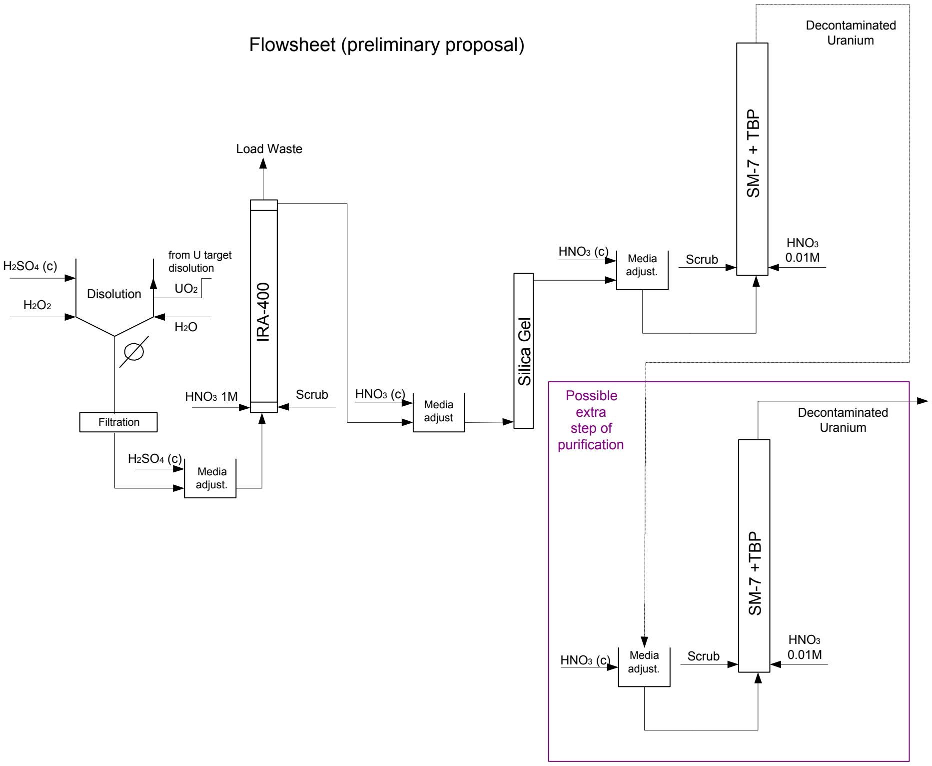

Figure 3: Flowsheet (Preliminary proposal)

Tests

Since the uranium purification must be performed in a hot cell, simplicity of design and operation is desirable. For this reason, fixed bed operations are the preferred alternsative.

Two different techniques for uranium decontamination have been studied:

- Uranium purification by ion exchange in a bed of anionic resin Amberlite IRA-400.
- Uranium purification by chromaytographic extraction in a bed of TBP-inert support material. The support material was BioRad Bio Beads SM-7

In addition, a technique for Zr-Nb separation was also considered: Zr-Nb retention in silica gel.

The tests were divided into two stages:

- Inactive tests involving natural uranium and tracers (inactive and active).
- Active tests employing the actual plant solutions.

At this moment, the first stage is almost complete. The tests with active tracers are currently being prepared and will be completed in a short time. The second stage would require the adaptation of the process to hot cell operation, and its continuation will be decided in the future.

Tests with natural uranium

Batch experiences for the determination of the equilibrium were done with both the anionic resin and TBP/SM-7. The U equilibrium results for the latter are in good agreement with the predictions of the equilibrium correlation employed by the Sephis 3 code (8) (Figure 3B).

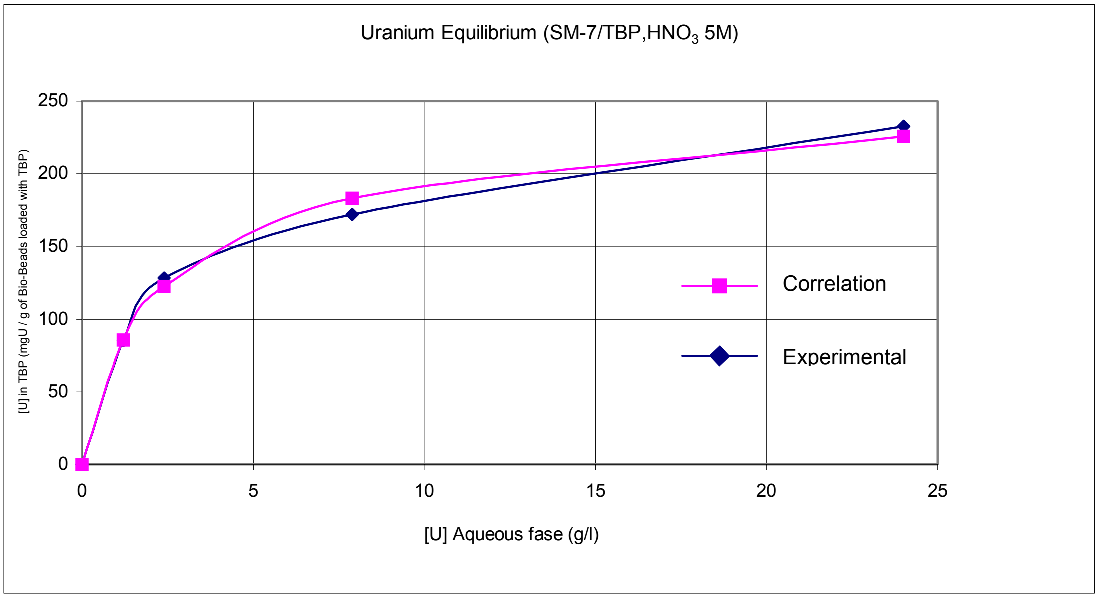

Figure 3B . Comparison between experimental and predicted equilibrium data.

For the column tests a device based on a Mariotte flask was selected to feed constant flow rates to the solutions. This device could be adapted to hot cell operation because is has no mobile parts.

After several runs the operative conditions for the anionic resin bed and the chromatographic extraction column summarized in the next table were selected:

Operation	**Ion Exchange**	**Chromatographic Extraction**
Flow Rate	1.7 column volumes (CV) / h	2.1 CV / h
Composition of the Feed Solution	Uranium: 5-30 g/l Sulfuric acid: 0.25 M	Uranium: 15-20 g / l; Nitric acid: 2-5 M.
Composition of the Scrubbing Solution	Sulfuric acid: 0.25 M.	Nitric acid: 2-5 M.
Composition of the Elution Solution	Nitric acid: 1 M.	Nitric acid 0.01 M

In the extraction tests the column capacity was close to the theoretical value (based on the equilibrium isotherm and the amount of TBP in the column). The mass transfer zone was short, the uranium loss during the loading and scrubbing stages was small, and the uranium concentration in the product was high enough for it to be fed (after adjusting its acidity) to a second extraction column, if additional purification stages were necessary.

The behavior of the anionic exchange column was also satisfactory, but with a real column capacity well below the theoretical value, due to a larger mass transfer zone. This would mean bigger columns, which is a drawback because of the space limitations inside hot cells. The uranium concentration in the product was also lower than in the extraction column. If the product were processed in an extraction column for additional decontamination, the capacity of that column would be limited by the lower feed stream concentration.

Tests with inactive tracers

Different simulant solutions containing uranium and low concentrations (~1 ppm) of Cs, Ba, Sr, Sb, Zr, Nb, Ru y Ce were prepared to evaluate the decontamination of the main fission products achievable with the processes under study. The concentrations were selected in order to work in the linear zone of the equilibrium curve (constant distribution coefficients), so that the results would be extrapolable to the actual operation. Since most samples from the experiences would have concentrations up to three orders of magnitude lower than the feed stream (ppb) it was decided to analyze them by ICP-MS.

The solutions were heated at boiling temperature for a few hours attempt to have the elements in the same chemical form as in the real solution.

Besides the TBP and ion exchange column tests, batch equilibrium tests with silica gel were conducted in order to establish the distribution coefficients of the fission products. The initial concentration was: nitric acid: 2 M; uranium: 10-15 g/l; tracers:~1 ppm.

Results and Discussion

Figure 4 shows the concentrations of uranium and tracers (divided by the feed concentration) at the exit of the IRA-400 column versus the column volumes. The load , scrubbing and elution stages are represented. The column capacity, the product uranium concentration and the separation of the uranium from tracers such as Cs, Sr and Ce were acceptable. However, the decontamination of the other PFs, especially Zr and Nb, was insufficient. The high DF for Zr is mentioned in (6).

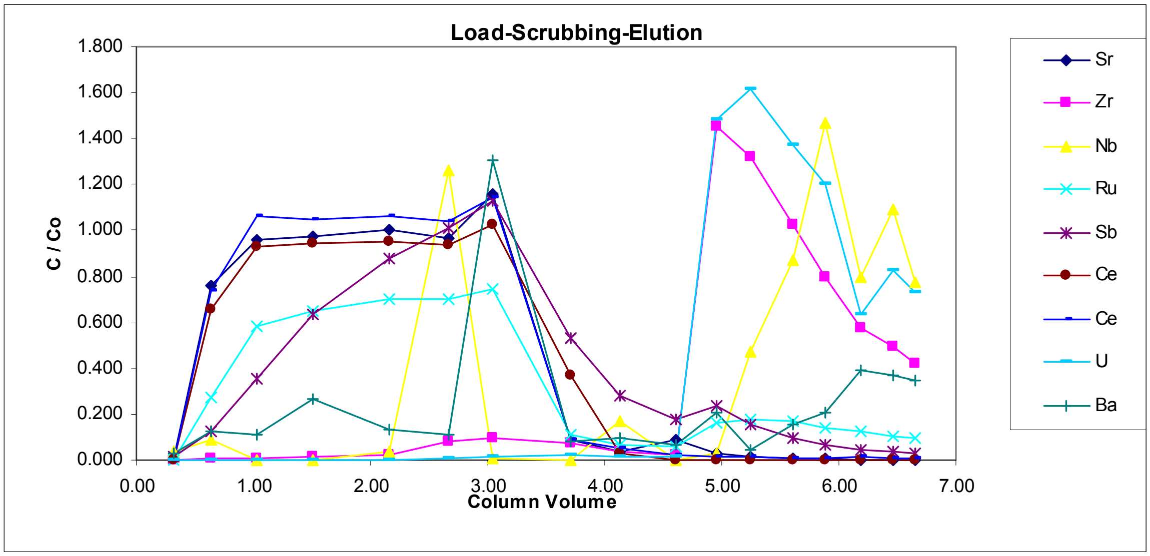

Figure 4: output concentration of uranium and tracers in an experience with an anionic exchange resin bed. Load step: 0-2.6 CV. Scrubbing step: 2.6-3.8 CV. Elution step: 3.8-6.6 CV.

The complexity of the curves for some elements suggests the presence in the solution of several compounds of the same element with different distribution coefficients.

The following table presents the decontamination factors of the tracers for both processes:

Decontamination Factors		
Element	**IRA-400**	**TBP**
Sr	32	390
Zr	1	418
Nb	2	62
Ru	7	116
Sb	6	510
Cs	127	566
Ba	4	636
Ce	47	575

Figure 5 shows the concentrations of uranium and tracers (divided by the feed concentration) at the exit of the TBP column versus the column volumes. The stages of loading , scrubbing and elution are represented. The column capacity, the product uranium concentration and the separation of the uranium from all tracers were very good.

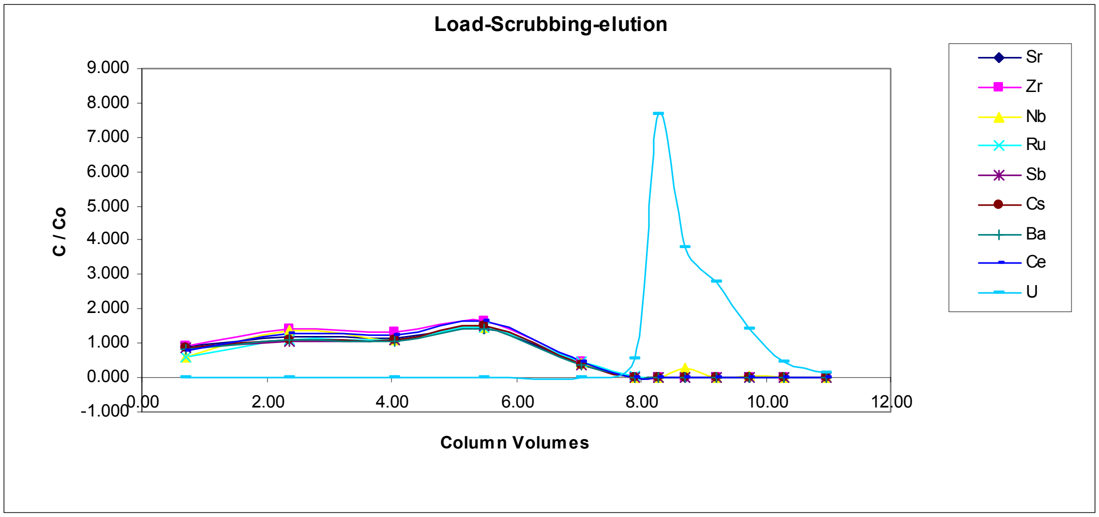

Figure 5: output concentration of uranium and tracers in an experience with a chromatographic extraction bed. Load step: 0-6.2 CV. Scrubbing step: 6.2-7.4 CV. Elution step: 7.4-11 CV.

The silca gel showed a high distribution coefficient (~1000) for Nb. The results for Zr were not conclusive and further tests will be conducted with active tracers. Nevertheless, the result for Nb would probably justify by itself the use of a silica gel bed to complement the solvent extraction process.

Modeling

A physical model of the SM-7/TBP column behavior was developed. This model considers axial dispersion and local equilibrium for the multicomponent system. It includes the U-nitric acid-TBP system equilibrium taken from the Sephis 3 code, and correlations for the Zr, Nb and Ru equilibrium. The physical model leads to a system of partial differential equations which are solved by numerical methods. The computer code is currently being tested. It will be used as a complement of the experimental results in the determination of optimal operative conditions for that process.

Conclusions

The performance of the TBP column, even with elements that are extractable in TBP, such as Zr, Nb and Ru, was superior to that of the ion exchange column. These results are consistent with the preliminary predictions obtained from the computer model of the chromatographic extraction. However these results should be considered preliminar, because the chemical form of the elements employed as tracers may not be the same as in the actual solution.

The results of the tests with active tracers suggest that chromatographic solvent extraction should be selected as the preferred method for uranium decontamination, using two columns in series if necessary. A silica gel bed could be adopted if the decontamination of Zr and/or Nb needs to be improved.

The forthcoming active tests will help to better define the process.

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