STUDY OF ALUMINA USE AS A SEPARATION STEP IN MO-99 PRODUCTION

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Abstract

The known use of alumina as a separation step of ^{99}Mo in acid medium requires, for its proper accomplishment, the determination of both the type of alumina and the separation conditions. Utilization of LEU can involve changes in the nature of the targets and also in the dissolution method, which necessitates the eventual consideration of an acid medium for the attack. A study on molybdenum retention and elution in alumina was performed at laboratory scale, using ^{99}Mo radiotracer. Different kinds of alumina were tested for varying conditions (acidity, temperature and uranium concentration) of the loading solutions. The behaviour of uranium in this proposed separative stage was also studied.

Introduction

Technetium-99m, product of radioactive decay of ^{99}Mo, is the most widely applied radioisotope in nuclear medicine. Since 1985 the Argentine National Atomic Energy Commission (CNEA) has been producing, in a routinely form, ^{99}Mo by fission of high-enriched uranium (HEU) in targets that are irradiated in its RA-3 reactor [1-2]. Due to nuclear-proliferation considerations and the running off the HEU inventory, these targets will be replaced

for others with low-enriched uranium (LEU). In this sense Argonne National Laboratory (ANL) is transferring the technology for the production of targets containing uranium metal foils.

Although at the present time, the irradiated targets are dissolved in basic medium, acid dissolution could be more suitable for the new ones, if the additional objective of separating other fission products is included. Use of alumina as a first separation step in acidic-processes is applied by some ^{99}Mo producer countries [3-5]. However, a complete study, in order to determine the alumina type and the most convenient operational conditions, becomes necessary.

The present work describes the experiments performed to test the influence of pH, uranium concentration, temperature and loading velocity, on the molybdenum retention in different aluminas. The uranium behaviour along molybdenum separation in alumina, was also studied.

Experimental

Molybdenum retention in aluminas of different characteristic and trademarks was initially studied, varying the acidity of the loading solution. A group of aluminas (Al_2O_3) for chromatography: Acidic-Fluka, Weakly Acidic-Fluka, Neutral-Fluka, Neutral-Merck, Acidic Super1-ICN, and Basic Super1-ICN, all them sifted (mesh < 200), were used. The loading solutions were prepared with 170 mg U/mL, ^{99}Mo radiotracer, and molybdenum carrier (0.068 mg/mL, which correspond to a concentration of 0.4 mg Mo per gram of U) in different nitric acid concentrations.

In this stage, as well as in the whole work, the experiments were carried out using 10 ml of the loading solution and a column containing 2 g of Al_2O_3 , with 5.6 cm height and 0.7 cm internal diameter ($h/\phi = 8$). The initial ^{99}Mo activity, the loading wastes and the washing solutions (HNO_3 1M, H_2O, and NH_3 0.01M) were measured either with an ionisation chamber or a NaI(Tl) detector associated to a multichannel analyzer. The percentages of molybdenum retention were calculated from these data. Unless otherwise stated, the loading velocity was in 7 cm/min.

The next stage was the study of the influence of uranium concentration in the loading solution over molybdenum retention. Four different branches of alumina (Acidic-Fluka, Weakly Acidic-Fluka, Neutral-Fluka, Acidic Super1-ICN) were tested with loading solutions having

different concentrations of uranium, molybdenum carrier (0.4 mg/g U) and ^{99}Mo radiotracer. The pH of all the solutions was 1.5

The influence of the increasing of temperature in the loading solution on the molybdenum retention in alumina was also studied. The experiments were carried out with the said aluminas and loading solutions with 170 mg uranium per millilitre (pH = 1.5), ^{99}Mo radiotracer and Mo carrier (0.068 mg/mL). In these cases, the solution was heated and then passed through the column at 40-45°C.

The influence of the loading velocity on the molybdenum retention in alumina was also analysed. For this, two aluminas (Acidic-Fluka and Neutral-Fluka) were employed; the solutions had characteristics similar to those described before and the loading velocities were 3.9 cm/min and 8.8 cm/min.

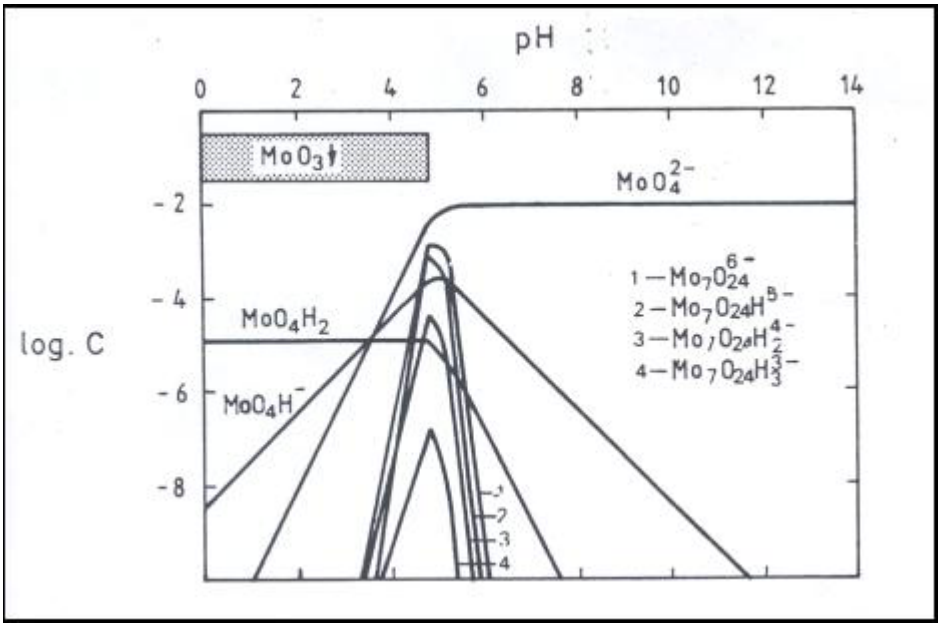
In addition to the studies involving the loading and washing solutions, the characteristics of the molybdenum elution were studied, using different volumes of 1M and/or concentrated NH_3. Two elution curves were performed, using respectively 4.4 ml and 8.5 ml of concentrated NH_3, collecting in both cases aliquots of approximately 0.65 ml. The eluted fractions were measured as it was described in previous paragraphs, and the elution percentages were calculated.

The behaviour of uranium along the molybdenum separation was studied with a weakly Acidic – Fluka alumina and a 170 mg U/mL loading solution (pH = 1.5), settling the passage through the column at 3.9 cm/min velocity. The column was washed three times, respectively with 0.8 mL HNO_3 1M, 1.7 mL H_20 and 1.7 NH_3 0.01M. Then the elution solution (4.4 mL of concentrated NH_3) was collected in three fractions. The uranium present in the loading waste, and both the washing and the elution solutions were measured, depending on the concentration, by redox potenciometric (Davies & Gray modified method) or absorption molecular spectrometry with DBM.

Results and Discussion

Molybdenum is an element belonging to the group VI of the periodic chart, with oxidation states: (II), (III), (IV), (V), and (VI). The last one is the most abundant and stable because of its charge/ radius relationship. As it is shown in the species diagram, picture 1 [6], the

possible species at pH = 1.5 are MoO_3, H_2MoO_4 and $HMoO_4^-$. However, molybdic acid polymeric anions could exist in slightly acid solutions [6-7]. For high acid concentrations, the oxidation state (V) either as MoO_2^+ or MoO^{+3}, is probable [8]. The eventual occurrence of important radiolisis effects caused by the high radiation field during a ^{99}Mo production process can not be discarded. If such possibility is admitted, part of the molybdenum present would appear in a reduced state, so that different species with oxidation state (V) will be found, together with some others having oxidation state (VI), and even mixtures of species of both states, which are denominated "blue oxides". All these facts will demand the future characterization of the involved species in the ^{99}Mo production process, and also to establish if a procedure destined to assure the presence of one particular chemical form will be required.



Picture 1. Log C vs pH diagram, for molybdenum (VI) 10^{-2} M [6]

The above considerations are applicable to this work, since ^{99}Mo from different origins presented different results for identical tests. Thus, the study of variables on the molybdenum retention presented in this work , has the only purpose of a comparative analysis.

In the experiments of molybdenum retention it was observed that for any of the tested aluminas the influence of pH was similar, the best results corresponding to 0.1M and 0.03M [H^+] concentrations. It can be seen in figure I that four aluminas (Acidic-Fluka, Weakly Acidic-Fluka,

Neutral-Fluka, Acidic Super1-ICN) out of the six used in the experiments showed higher retention percentages. These aluminas were selected to be used in the following stages of the study. The most favourable pH is 1 for Acidic-Fluka and the Acidic Super1-ICN aluminas, whereas both the Weakly Acidic-Fluka and the Neutral-Fluka aluminas show better performances at pH = 1.5. All the same, the differences in the molybdenum retention in any of the aluminas are less than 2% for 1 to 1.5 pH range. This fact allows to establish this as a working range for the loading solution.

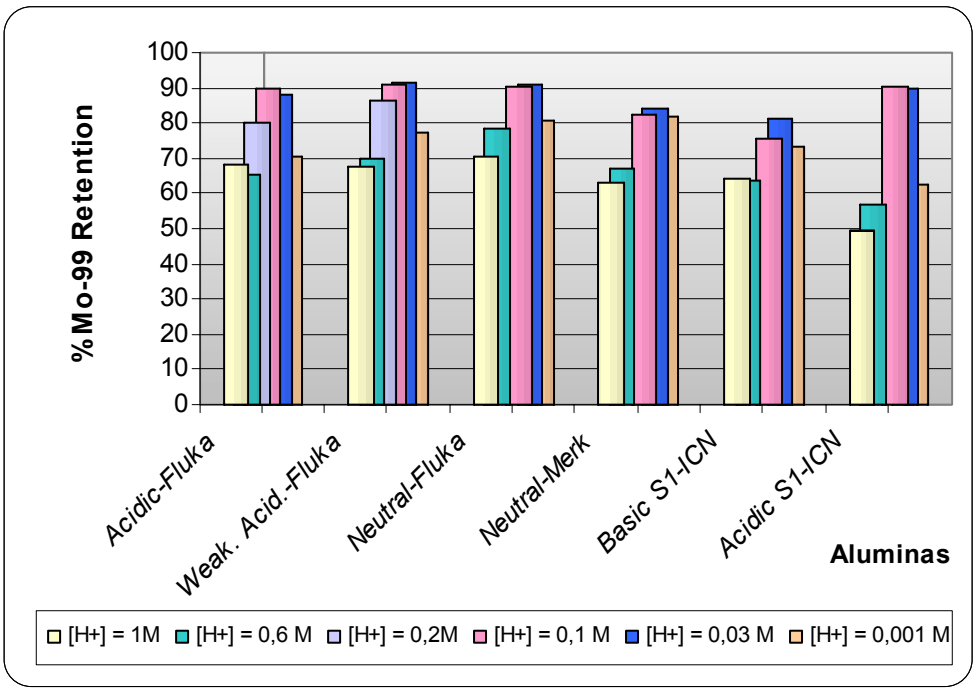


Figure I. Molybdenum retention in different kinds of aluminas varying loading solution acidity

The influence of uranium concentration in the loading solution over molybdenum retention in different aluminas was analysed (Figure II). It can be observed that molybdenum retention always diminish when uranium concentration increases. These results allow to outline the compromising situations, where it is advisable to diminish the uranium concentration, thus increasing the volume of the loading solution and the size of the column.

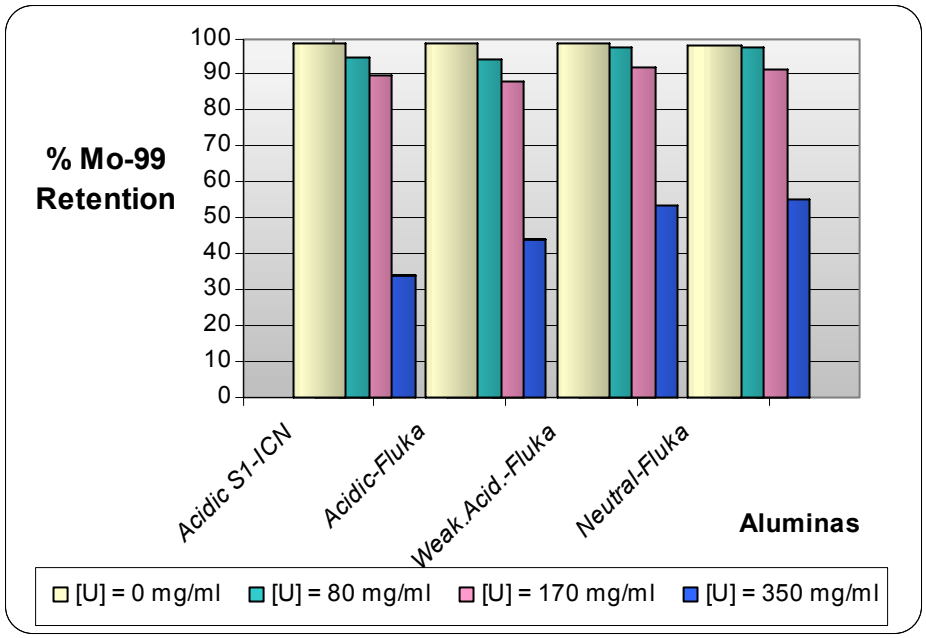


Figure II. Molybdenum retention in different kinds of aluminas varying uranium concentration in loading solution.

In figure III some of the data obtained in the previous stages are compared with the results found under the same conditions, with the only exception of the temperature of the loading solution, which in this case was within 40-45°C. The increase of temperature results in a drop of molybdenum retention.

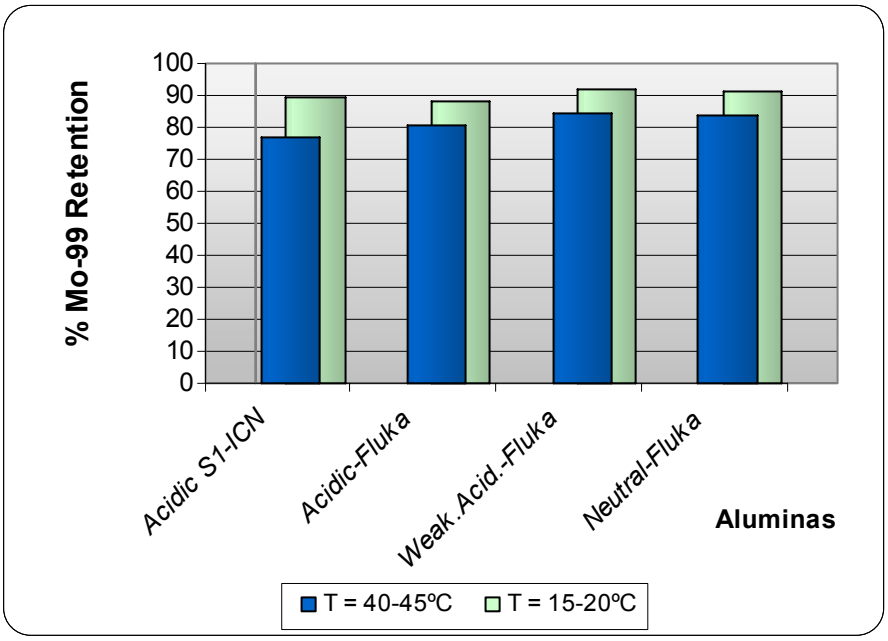


Figure III. Molybdenum retention in different kinds of aluminas varying temperature in loading solution

With respect to the influence of the loading velocity on the molybdenum retention in the alumina column, the results show an increase of 2 - 9%, depending on the alumina, when diminishing the passage velocity to 3.9 cm/min; a decrease of the same magnitude was observed when the passage velocity was increased to 8.8 cm/min.

No significant differences were found among the tested aluminas in connection with molybdenum elution. From all the elutions tested the best yields were obtained with concentrated NH_3 (≥ 80%). Figure IV shows a complete elution curve obtained by passage of 8.5 mL of concentrated NH_3 with recollection of the eluate in small fractions. The elution yield reached 86% of the retained molybdenum. As it had already been observed in other tests and confirmed in this figure, there is a possibility to discard the first two recollections, since they contain < 1% of the retained molybdenum. In the same way, it is possible to consider the diminishing of the elution volume to 5.2 mL since the activities, from this upper limit, do not exceed 1% of the retained molybdenum.

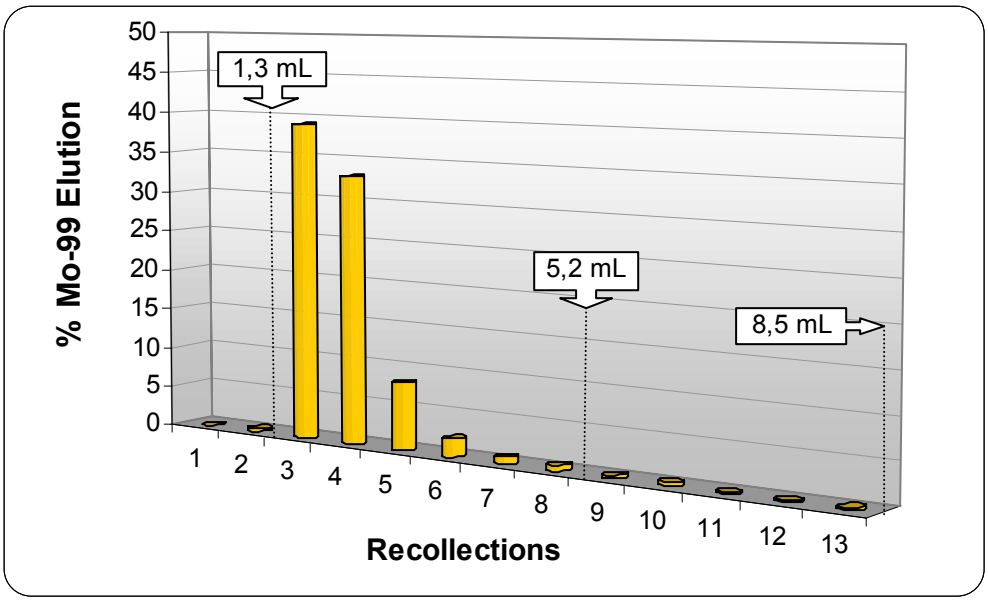


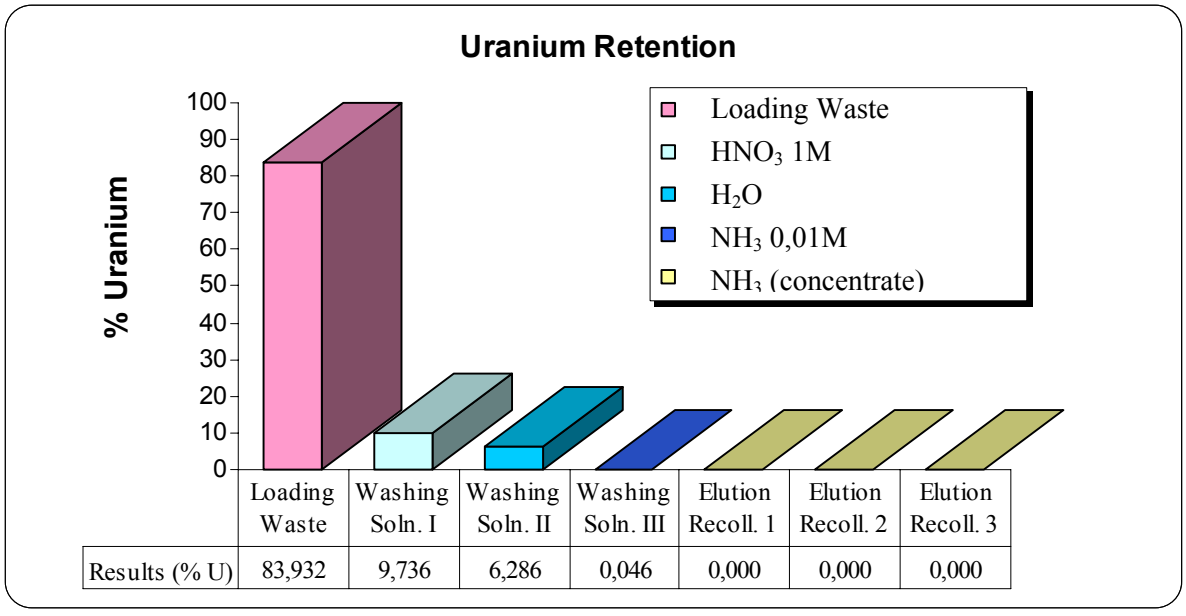
Figure IV. Elution curve of molybdenum retained in alumina.

The experiments carried out in laboratory scale with radiotracers allow to calculate in estimative way column dimensions, time of loading passage and elution volumes that would be required for this purification stage in a production process.

A productive process is considered where a total mass of 120 g of irradiated uranium metal foil would be dissolved with acid solution (HNO_3) and the following parameters are either fixed or calculates:

- *Uranium concentration fixed as 150 g/L*, which allows an appropriate molybdenum retention in the alumina, and corresponds to loading *volume = 800 mL.*
- Constant mass/volume relationship, the *minimum alumina mass being 160 g.*
- This alumina mass corresponds to a column volume = 172 cm^3, which implies a column *height = 24 cm* and *internal diameter = 3 cm* ($h/\phi = 8$).
- *Loading velocity of 3.9 cm/min*, calculated *flow = 27.57 mL/min* and total time involved in the passage *t = 29 min.*
- Finally, a calculated elution passage of *416 mL of concentrated NH_3*, with recovery of the last *312 mL of the eluate*.

The results of uranium behaviour in this molybdenum separation step are summed up in figure V. Most of the uranium was lost in the loading waste. These tests confirmed the utility of the different washings, since the subsequent elutes are free of uranium



	Loading Waste	Washing Soln. I	Washing Soln. II	Washing Soln. III	Elution Recoll. 1	Elution Recoll. 2	Elution Recoll. 3
Results (% U)	83,932	9,736	6,286	0,046	0,000	0,000	0,000

Figure V. Uranium retention in weakly acidic- Fluka alumina

Conclusions

In spite the fact that the method studied is already known, the characterisation accomplished in the present work allowed to select the aluminas with better molybdenum retention percentages, and the best loading conditions corresponding to pH between 1 and 1.5. The factors that diminish the molybdenum retention are the presence of uranium, the increase of the temperature and the loading velocity.

The importance of the different washings to entirely remove the uranium present was demonstrated.

The possibility of using concentrated NH_3 for the elution of the molybdenum retained in alumina was proved; the results also showed the viability of discarding the first fractions of the eluting volume.

The obtained data allowed the estimation of the conditions for ^{99}Mo retention to an industrial scale.

Acknowledgements

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