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PROPOSAL OF A SEPARATION PROCESS FOR THE PRODUCTION OF Mo-99

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ABSTRACT

This work is a partial result of the separation and purification process study of fission ^{99}Mo which is inserted in the research of production technology of ^{99}Mo by alkaline dissolution of UAl_x-Al targets at the IPEN/CNEN-SP. Anionic exchangers Dowex 1x8 and AG 1x8, and acidic and neutral aluminas were evaluated on Mo removal from an alkaline solution containing Al ions by batch/column assays. No Al influence was observed on Mo adsorption. Two columns were placed in series, one containing a bed of Dowex 1x8 and another containing bed of acidic alumina, and an alkaline solution containing Al ions and Mo ions was percolated through the Dowex 1x8 column to Mo retention. Then, Mo was eluted and collected into the outlet vial; it was acidified and percolated through the second column of acidic alumina, and eluted with NH_4OH. The final recovery of Mo was of 90.2% without Al contamination indicating high performance and application perspective of the process for production technology of fission ^{99}Mo.

1. INTRODUCTION

Technetium-99m, ^{99m}Tc, the short lived daughter product of the ^{99}Mo, is the radioisotope most widely used in nuclear medicine as radioactive tracer of several radiopharmaceuticals. This single isotope is used in over 80% of all diagnostic procedures. In recent years, Brazil started the Brazilian Multipurpose Reactor project (RMB) whose main objective is the production of 1000 Ci/week of fission ^{99}Mo for national demand and to ensure a stable domestic supply of ^{99m}Tc in the next decade. At present the ^{99m}Tc domestic supply is dependent on the import of the ^{99}Mo radioisotope. This work is part of the RMB research project to separate and purify the ^{99}Mo fission by chromatographic columns from alkaline dissolution of UAl_x-Al targets of low enriched uranium (LEU). After irradiation in reactor, uranium targets are dissolved by acid or alkaline solutions, and the resulting solution goes through a series of chromatographic columns that allows a gradual decontamination of other components, yielding the ^{99}Mo with high radiochemical and chemical purity for use in nuclear medicine as generator of ^{99m}Tc. The work began in 2010, where alkaline dissolution of Al plates and process of separation and purification using ^{99}Mo tracer is being held at the Environmental Chemistry Center (CQMA), IPEN/CNEN-SP. The first papers were presented

on the 32nd International Meeting on Reduced Enrichment for Research and Test Reactors-RERTR 2010 [1, 2] and others more recent can be found in references [3-6]. In this paper, anionic exchangers Dowex 1x8 and AG 1x8 and the adsorbents acidic alumina and neutral alumina were investigated on Mo removal from an alkaline solution containing Al ions by batch assays and a separation process in column was proposed. These materials are generally used in the production chemical processing of fission ^{99}Mo from alkaline dissolution of U targets around the world [7, 8].

2. EXPERIMENTAL

2.1. Material

Molybdenum stock solution was prepared by the dissolving of $Na_2MoO_4.2H_2O$ in distilled water. Aluminum solutions were prepared by dissolution of aluminum plates in boiling 3 mol.L^{-1} NaOH solution. The plates were made of aluminum 6061 at the CCN-IPEN/CNEN. Dowex 1x8 resin (Sigma-Aldrich) and AG 1x8 resin (Merck), < 100 mesh, and were worked as received. Acidic alumina and neutral alumina (Merck), < 100 mesh, were used no preconditioning. The aluminas were worked as received. Other used chemical reagents were analytical grade. The ^{99}Mo tracer solutions were provided by the CR-IPEN/CNEN.

2.2. Batch Assay

Adsorption experiments were conducted by the batch assay. Fifty milligrams of Dowex 1x8 resin was placed in contact with 1 mL of aluminum solution containing 0.5 or 30 mg. L^{-1} Mo and ^{99}Mo tracer, in the stirring at 200 rpm, for 40 min on a shaker Q225M, Quimis. After the contacting, a volume of the supernatant was removed and centrifuged on a Quimis 222T for separation of suspended particles. Supernatant aliquot was counted at the energy of 739 keV using an HPGe detector, Canberra, at the CR-IPEN/CNEN. An aliquot of initial solution of Mo was also counted. The same batch procedure was carried out with AG 1x8 resin and aluminas. The counts of the supernatant and the initial solution were correlated to the Mo concentrations. Adsorption efficiency of adsorbents was evaluated based on the percentage values of removed Mo from aqueous phase calculated according to the equation (1).

$$\text{Adsorption \%} = (1 - (C_a / C_b)) \times 100 \qquad (1)$$

Where: C_a = gamma counting rate of the supernatant (after contact)
C_b = gamma counting rate of the initial solution (before contact)

2.3. Procedure for Column Operation

Two glass chromatographic columns with 10 mm internal diameter, one containing a 100 mm bed of Dowex 1x8 and another containing a 104 mm bed of acidic alumina, were placed in series. An alkaline solution (50 mL, pH 14 and 39.4 g.L^{-1} Al) prepared by dissolution of Al plates, not irradiated, with 3 mol.L^{-1} NaOH, and containing 5 mg.L^{-1} Mo (with ^{99}Mo tracer)

was percolated through the Dowex 1x8 column to Mo retention. After the column washing with 50 mL of 1 mol.L^{-1} NaOH solution and 50 mL of distilled water, the Mo was eluted with a 1 mol.L^{-1} NH_4HCO_3 solution, and collected into the outlet vial. This eluted solution was acidified with 12.9 mol.L^{-1} HNO_3 and percolated through the second column of acidic alumina. After the washing through with 50 mL distilled water and 50 mL of 0.01 mol.L^{-1} NH_4OH, the Mo was recovery by elution with a solution of 1 mol.L^{-1} NH_4OH. The flow rate was maintained at approximately 2 mL.min^{-1} throughout.

3. RESULTS AND DISCUSSION

3.1. Influence of pH, Al Ions and NaOH Concentration

In alkaline dissolution process of UAl_x-Al targets with NaOH, the resulting dissolution solution of pH ~14 contains large amount of aluminate anions, $[Al(OH)_4]^-$, and fission ^{99}Mo as molybdate anions, MoO_4^{2-}. And of course the dissolution solution contains too other fission products (~64%) together with small amounts of U and minor actinides (transuranic). So, the understanding of the adsorption and desorption behaviors of molybdate anions on the anionic exchangers Dowex 1x8 and AG 1x8, and on the adsorbents acidic alumina and neutral alumina is very important to order to propose a separation and purification process of fission ^{99}Mo by chromatographic columns.

Firstly, Mo solutions of pH from 0.5 to 14 were prepared, and were contacted with the chromatographic materials in according the batch procedure. The result is showed in Fig. 1 whose adsorption behavior on the Dowex 1x8 and AG 1x8 indicated that in the range from 3.0 to 12.5 the Mo adsorption is highly favorable with more 99.8% adsorbed. From the pH 13.0, the Mo adsorption decreased to achieve 72.5% at pH 14. On the aluminas, the adsorption is highly favorable in the studied acidic pH and alkaline pH up to 10.

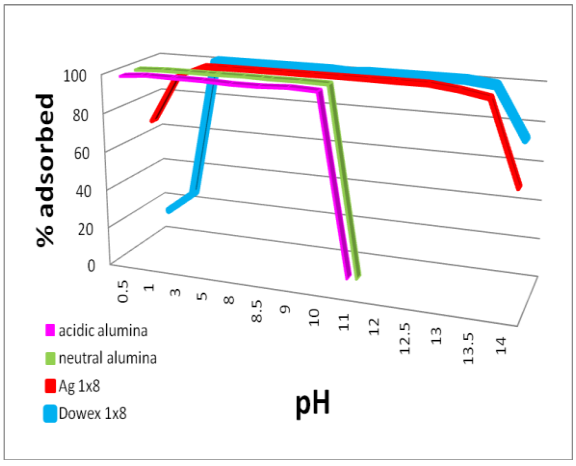

Figure 1. Adsorption of MoO_4^{2-} anions from the acidic and alkaline solutions on the anionic exchangers and on the aluminas at 27±1°C. Initial concentration of Mo = 0.5 mg.L^{-1} for acidic alumina, neutral alumina e Dowex 1x8 resin and Mo = 30 mg.L^{-1} for AG 1x8 resin.

This result shows that the fission ^{99}Mo adsorption from a alkaline dissolution solution of pH 14 will occur only on the Dowex 1x8 or Ag 1x8. The adsorption on the aluminas will be possible only after an acidification of the alkaline dissolution solution as is made in the ROMOL process [8].

But the acidification process of alkaline solution containing Al ions as the alkaline dissolution solution of UAl_x-Al targets is not easy. The Al ions hydrolyze and solidify in solution of pH from ~3 to ~12. In the high concentration, the hydrolyzed Al ions are bulky occupying large space and difficulting the stirring of the acidification process until to reach pH < 2. Furthermore, the global processing time will increase, what is not recommendable to the production of fission ^{99}Mo.

The influence of Al ions and concentration of NaOH solution on adsorption of Mo ions on these chromatographic materials was investigated. Three solutions of aluminate anions were prepared by the dilution of the dissolution solution of Al plates (not irradiated) with NaOH, and molybdate anions were added, and were submitted to the batch assays. The result is showed in Fig. 2.

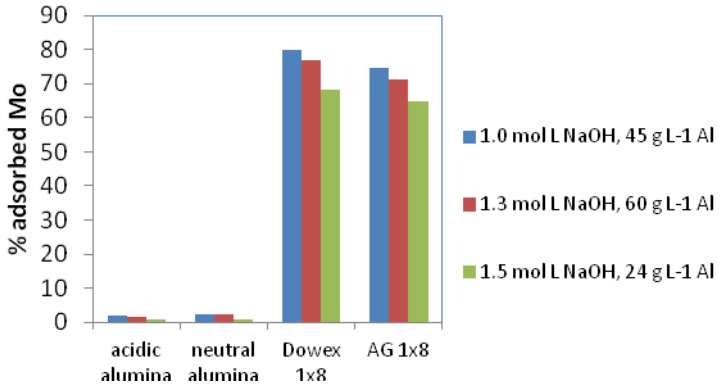

Figure 2. Adsorption of MoO_4^{2-} anions from the alkaline solutions on the anionic exchangers and on the aluminas at 27±1ºC. Initial concentration of Mo = 25 mg.L^{-1}.

Fig. 2 shows that the Mo adsorption is high on the anionic exchangers and no influence was observed with the increasing of the aluminate concentration up to 60 g.L^{-1}. Between two anionic exchangers, adsorption was 4% higher on the Dowex 1x8.

On the other hand, the increasing of the NaOH concentration from 1.0 mol.L^{-1} to 1.5 mol.L^{-1} decreased the Mo adsorption on the anionic exchangers up to ~10%. This result was waited in agreement with the pH study showed in Fig.1. The increasing of NaOH concentration increases the OH^- anions concentration, therefore increases the pH value.

For aluminas the Mo adsorption is very low in high pH independent of Al ions as show Fig. 2. The Mo is adsorbed on the aluminas only in pH lower 10 as showed in Fig.1. More information about the adsorption behavior of Mo on anion exchangers and aluminas from aluminate ions solutions and pH can found in the references [4, 9].

3.2. Dowex 1x8 and Acidic Alumina Columns

Based on the studies of pH/Al, the eluents presented by Damasceno et al. [9], and considering the alkaline dissolution solution of ^{99}Mo with large amount of Al, this work has proposed a process of separation and purification of fission ^{99}Mo. In these conditions, the process has consisted of a Dowex 1x8 column followed of another acidic alumina column, and as eluents of Mo, the NH_4HCO_3 and NH_4OH solutions were considered, respectively.

A load-solution was prepared from the alkaline dissolution solution of the Al plates, and all column operation was carried out as described in item 2.3. More than 99.9% of Mo was retained on the Dowex 1x8 column, and none Al was retained. The Al presence was systematically monitored by acidification assays of effluent. One washing of the Mo-loaded column was carried out by passing of NaOH solution until to confirm the Al absence in the wash solution. A second washing was done with distilled water in order to clean the NaOH of the column, and to prepare it to receive the eluent NH_4HCO_3.

Fig. 3 shows the Mo elution profile from the Dowex 1x8 column with NH_4HCO_3. The elution initiated rapidly, and the maximum elution point occurred at 40 mL of NH_4HCO_3. An efficiency of 99.8% for Mo removal with 97 mL of NH_4HCO_3 was obtained.

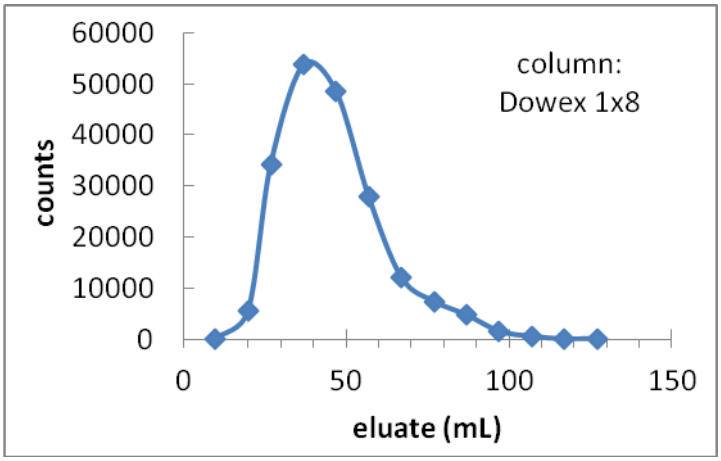

Figure 3. Molybdenum elution profile from the Dowex 1x8 column (bed = 5.80 g) with 1 mol.L^{-1} NH_4HCO_3 solution. Load solution = alkaline solution (50 mL, pH 14) prepared by dissolution of Al plates with 3 mol.L^{-1} NaOH (39.4 g.L^{-1} Al), and containing 5 mg.L^{-1} Mo (added ^{99}Mo tracer). Flow-rate = 2 mLper min.

The eluted NH_4HCO_3 reacts with the alumina beads of the next column forming air bubbles, and furthermore the Mo is not adsorbed on the alumina from this medium. Therefore, this eluted was acidified before to pass through the alumina column. The acidification step destroys the carbonate anions and the ammonium cations resulting a final solution of acidity appropriated to adsorb the Mo. A final volume of approximately 99 mL of acidified eluate was obtained, which was passed through the alumina column.

The Mo-loaded alumina column was washed with distilled water to clean the acid medium and was also washed with diluted NH_4OH to prepare the alumina column for the Mo elution with 1 $mol.L^{-1}$ NH_4OH solution.

The Mo elution profile from the acidic alumina column is showed in Fig. 4, whose recovery in 20 mL of NH_4OH was of 90.2% in relation to the initially percolated Mo into the Dowex 1x8 column and loss lower than 0.01% was verified in all washing steps.

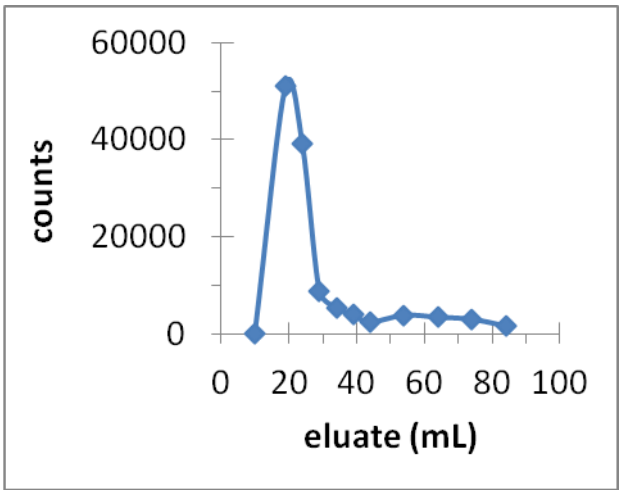

Figure 4. Molybdenum elution profile from the acidic alumina column (bed = 8.04g) with 1 $mol.L^{-1}$ NH_4OH solution. Load solution = Mo solution eluted from the Dowex 1x8 column, and acidified (pH 1-2). Flow-rate = 2 mL per min.

4. CONCLUSIONS

The study showed that aluminum ions from the dissolution of the Al plate in 3 $mol.L^{-1}$ NaOH do not interfere on the Mo retention on the Dowex 1x8 column. Al ions were not retained on the column. Elution of Mo with NH_4HCO_3 was highly efficient. The acidifying of the eluted solution was simple and effective, so that no Mo loss was observed during the Mo retention on the alumina column. The process composed of a Dowex column followed by an alumina column, and steps of elution with NH_4HCO_3, acidification and final elution with NH_4OH showed to be efficient with a final recovery of 90.2% Mo without contamination of Al. The proposed process showed application perspective for the separation and purification of fission ^{99}Mo from alkaline dissolution of U-Al targets with NaOH. In next study, the elements I, Ru, Te and Zr will be added into the alkaline dissolution solution of Al plates containing Mo, and this solution will be passed through the chromatographic columns of proposed process, and its performance will be evaluated

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