

**RERTR 2010 – 32nd INTERNATIONAL MEETING ON
REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS**

**October 10-14, 2010
SANA Lisboa Hotel
Lisbon, Portugal**

**STUDIES ON THE SEPARATION OF ⁹⁹MO FROM NITRIC ACID
MEDIUM BY ALUMINA**

M. Yamaura, A.A. Freitas, A.P.G. Yamamura, R.M.N. Tanaka, C.A.L.G. de O. Forbicini, R.L. Camilo and I.C. Araujo
Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN
2242 Prof. Lineu Prestes Avenue, São Paulo, CEP 05508-000 – Brazil

ABSTRACT

^{99m}Tc, the product of radioactive decay of ⁹⁹Mo, is one of the most used radioisotopes in nuclear medicine. The ⁹⁹Mo is produced mainly by fission of ²³⁵U targets HEU or LEU. After the dissolution of uranium targets, chemical process for the separation and purification is performed in chromatographic columns. This work presents a study on the behavior of ⁹⁹Mo removal by adsorption on acid and neutral alumina from nitric acid, which is the dissolution reagent for LEU targets in the Modified Cintichem Process. Adsorption kinetics in solution of HNO₃ and the influence of pH were investigated. It was also evaluated the adsorption of ⁹⁹Mo from nitric solutions containing uranyl ions.

1. Introduction

Technetium-99m, the product of radioactive decay of ⁹⁹Mo, is the most widely used radioisotope in nuclear medicine, which is used in over 80% of diagnostic tests, especially cardiology and oncology. Since 2009, the production of Tc-99m generators suffers a global crisis of supply. The raw material, the ⁹⁹Mo, is produced mainly by fission of ²³⁵U in the reactor and became scarce after the shutdown of the NRU reactor in Canada and HFR in The Netherlands due to technical problems, triggering the crisis. The two reactors account for 64% of world production. To meet demand, even in part, currently, Brazil imports the ⁹⁹Mo Argentina [1], South Africa and Israel. Therefore, the Brazilian government invests in domestic production with the construction of a research reactor suitable for the production of fission ⁹⁹Mo [2] and the Institute for Energy and Nuclear Research/National Commission of Nuclear Energy (IPEN/CNEN) develops the production technology of ⁹⁹Mo from uranium LEU (low enriched uranium) targets (UAl_x/Al or metallic uranium). After irradiation of the U targets in the reactor, the process of separation of ⁹⁹Mo from fission products begins with the acidic (metallic uranium) or alkaline (UAl_x/Al) dissolution of the targets. 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 as generator of Tc-99m in nuclear medicine.

Due to its high selectivity for ^{99}Mo , alumina, Al_2O_3 , is widely used as adsorbent in chromatographic purification step in the alkaline dissolution process. Alumina is also used in the separation of ^{99}Mo from uranium and fission products in the dissolution of HEU targets (high-enrichment uranium) in nitric acid [3, 4].

In 1996, an acid dissolution of metallic uranium LEU targets, in the process called Modified Cintichem, was successfully demonstrated by Leonard et al. [5], who used nitric acid as a dissolution reagent instead of a mixture of acids. The main advantage in using only nitric acid is related to the treatment and disposal of radioactive waste, showing a significant reduction of the total cost of processing [6].

This work is part of a research for the development of ^{99}Mo production process from uranium targets where all the steps, from dissolution throughout separation and purification, are being investigated. The aim of this study is to evaluate the adsorption behavior of molybdenum by acid and neutral alumina from the acid dissolution of metallic uranium LEU targets with HNO_3 as the first separation step. The kinetics of adsorption, the influence of pH and the adsorption of Mo (VI) from nitric solutions containing uranyl ions were investigated.

2. Materials and methods

The Mo solution was prepared from the dissolution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in distilled water. The ^{99}Mo tracer and acidic and neutral alumina were provided by the Center for Radiopharmacy (CR/IPEN). The alumina was used without any pretreatment or conditioning. The uranyl ion solutions were obtained dissolving pure U_3O_8 with HNO_3 . Ammonium hydroxide p.a. and nitric acid p.a. were used in the experiments.

The adsorption assays of Mo ions from aqueous medium by alumina was performed by placing 1.0 mL of solution containing Mo and ^{99}Mo tracer in contact with 50.0 mg of alumina, at room temperature (Shaker mod. Q225M, and a tube centrifuge, Quimis). Mo solutions were prepared varying pH and uranyl ions concentration. After shaking at 200 rpm, the supernatant was separated and centrifuged for 3-5 min. A volume was removed and separated into another bottle to gamma counting at the energy of 739 keV in a Ge detector (Canberra). The experiments were performed in duplicate or triplicate and showed reproducibility greater than 90%.

The adsorption process was evaluated by distribution coefficient, K_d , defined in Equation 1.

$$K_d = ((A_i - A_f)/W)/(A_f/V) \quad (1)$$

Where A_i and A_f represent the activity (cpm) of the aqueous phase before and after contact, respectively, W is the dry mass of alumina (g) and V is the volume of the aqueous phase (mL).

3. Results and discussion

Figure 1 shows the adsorption kinetics of Mo (VI) at concentration of 0.07 g.L^{-1} in nitric acid solution with pH 1.1, represented by the variation of K_d with the contact time in acidic and neutral alumina in the range from 5 to 60 min. The higher the value of K_d , the greater the amount of ions of Mo (VI) adsorbed. A K_d greater than 2,000 means an adsorption of Mo greater than 99%. According to the kinetics, the adsorption increased with time to achieve equilibrium from 20 min, which is characterized by the curve plateau. The amount adsorbed is in equilibrium with the amount desorbed. The adsorption of Mo (VI) on alumina showed fast kinetics, which is a fundamental feature for chromatography in columns.

In subsequent studies, all adsorption experiments were performed using a contact time of 40 min to ensure the equilibrium time of Mo adsorption. The equilibrium time may vary due to the Mo concentration, temperature, adsorbent quantity or other assay conditions.

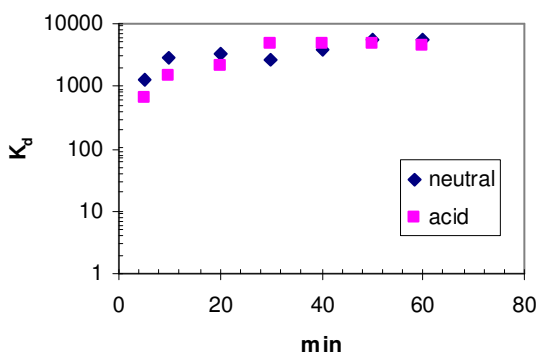


Figure 1. Adsorption kinetics of Mo (VI) (0.07 g L^{-1}) in acidic and neutral alumina from nitric acid medium, pH 1.1, at room temperature.

The adsorption of Mo (VI) in function of pH, in equilibrium, was evaluated and the result is illustrated in Figure 2. In acidic alumina, the existence of a pH range between 0.4 and 10.0, where the K_d value is greater than 479, peaking at 53,860, was verified. On neutral alumina, the maximum adsorption was found at pH 1.1 with K_d value equals to 3,742. At pH lower and higher than 1.1, adsorption decreased rapidly, but below pH 0.4 a K_d greater than in acidic alumina was observed. Mo (VI) in aqueous medium has several ionic species according to pH. At $\text{pH} < 1.0$, in which the concentration of H^+ is high, they form the neutral and cationic species. According to Olazabal et al. [7], the species existing in equilibrium are $\text{H}_6\text{Mo}_2\text{O}_8^{2+}$, H_3MoO_4^+ and H_2MoO_4 . Tangri et al. [8] suggest the predominance of MoO_2^{2+} and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. The low K_d value observed in Figure 2 at $\text{pH} < 1.0$ (acidic medium) indicates that the cationic species and neutral Mo (VI) have lower affinity for adsorption on acidic and neutral alumina.

Moreover, according to Olazabal et al. [7] and Tangri et al. [8], in $\text{pH} > 1.0$ anionic species are formed, such as $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$, $\text{Mo}_7\text{O}_{23}(\text{OH})_5^{5-}$, $\text{Mo}_8\text{O}_{26}^{4-}$, with predominance of MoO_4^{2-} at $\text{pH} > 6$.

Figure 2 shows that in the pH range from 1.0 to 10.0, the acidic alumina has high adsorptivity for the anionic species of Mo (VI). At $\text{pH} \geq 10.0$, the K_d values decreased markedly. In this case, it is suggested that the anions MoO_4^{2-} compete with the high concentration of OH^- ions by acidic alumina sites, resulting in low adsorption. This behavior suggests a process of desorption of molybdate ions from acidic alumina in an alkaline solution of $\text{pH} > 11.0$. For neutral alumina, Figure 2, the anionic species of Mo (VI), present at $\text{pH} 2.8$, showed a K_d value < 3 and, therefore, low adsorptivity. This confirms the same behavior observed by Bakel et al. (2006), where the K_d decreased with decreasing acidity from 0.1 to 0.01 mol.L^{-1} .

The acidic and neutral alumina showed high adsorption yield of Mo (VI) at acidic pH. However, the acidic alumina is applicable to both acidic and alkaline solution of ^{99}Mo between $\text{pH} 0.4$ and 10.0. The acidic alumina can be used for adsorption of ^{99}Mo when an alkaline dissolution of LEU targets is used. Neutral alumina can only be applied in acidic solutions, about $\text{pH} 1.1$.

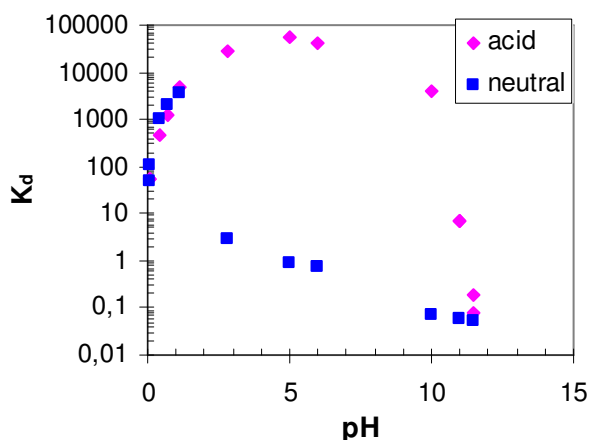


Figure 2. Adsorption behavior of Mo (VI) on acidic and neutral alumina from nitric acid medium at various pH. Equilibration time of 40 min.

To complement the study of Figure 2, the adsorption in the range of HNO_3 concentration from 0.5 to 2.0 mol.L^{-1} , i.e., below $\text{pH} 0.1$, was investigated. The results (Figure 3) show that the K_d value of Mo is low for HNO_3 concentration $> 1.0 \text{ mol.L}^{-1}$. The results confirm that the neutral alumina has a small advantage over the acidic alumina with respect to adsorption of Mo in the range from 0.5 to 1.0 mol.L^{-1} HNO_3 . Despite the low K_d value at 1.0 mol.L^{-1} HNO_3 , the adsorption of Mo is feasible in chromatographic columns for both adsorbents.

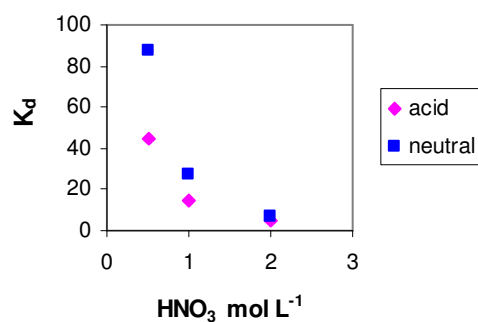


Figure 3. Adsorption behavior of Mo (VI) in acidic and neutral alumina with the concentration of nitric acid medium

In the Modified Cintichem process, the acid solution from the dissolution of LEU targets with HNO₃ contains uranyl ions, whose concentration is limited by the solubility of uranium, approximately 500 g.L⁻¹ [9].

The effectiveness of both alumina to adsorb Mo (VI) from uranyl nitrate solution, pH 0.4 and 2.8, was studied by varying the concentration of uranyl ions. The result is shown in Figure 4. At pH 0.4, it was found that the distribution coefficient K_d decreased sharply with increasing concentration of uranyl ions, significantly affecting the adsorption of Mo (VI) for both alumina. Considering only the value of $K_d = 40$ found in the studied conditions in a single equilibrium stage, the separation of Mo (VI) by adsorption on alumina proved to be viable in a maximum concentration of uranyl ions of 113.1 g.L⁻¹, when performed in chromatographic columns of several equilibrium stages. To confirm this assertion, it is necessary a detailed study on the adsorption behavior of Mo in the presence of uranyl ions in chromatographic column.

At pH 2.8 and absence of uranyl ions, where the adsorption of Mo reaches a K_d value equals to 27,380 on acidic alumina (a value much greater than on neutral alumina), in the presence of a increasing concentration of uranyl ions, K_d values decreased markedly. Above 26 g.L⁻¹ of uranyl ions, the K_d values were lower than those at pH 0.4. Therefore, separation of Mo (VI) in high concentrations of uranyl ions is better at pH 0.4 than at pH 2.8.

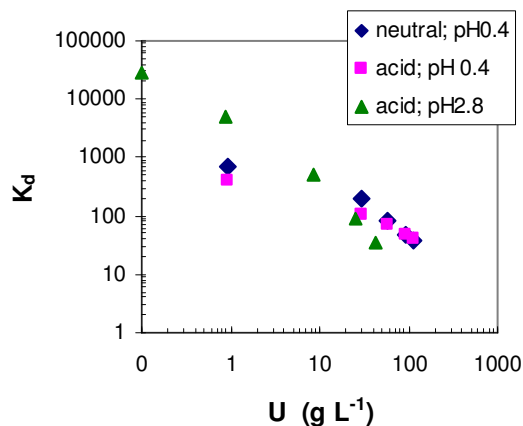


Figure 4. Influence of the concentration of U ions in the adsorption of Mo (VI) by means of alumina oxide at pH 0.4 and 2.8.

4. Conclusions

Under the conditions studied in this work, both acidic and neutral alumina can be used to adsorb ⁹⁹Mo depending on pH of nitric solution. The acidic alumina showed higher adsorption performance of Mo (VI) from nitric acid medium at a higher pH range, from 1.0 to 10.0, than neutral alumina. The neutral alumina showed high adsorption efficiency at pH near 1.0. The presence of uranium affects the adsorption of Mo by alumina, however, the K_d values indicate a possible separation of Mo at concentrations below 113 g.L⁻¹ of uranyl ions in chromatographic columns. Future work for the separation of Mo from U solutions in chromatographic columns is programmed with the acidic and neutral alumina.

5. References

- [1] S. BALART, P. CRISTINI, A.G. GONZALEZ, R. GONZÁLEZ, J.D. HERMIDA, M. LÓPEZ, M. MIRANDOU, H. TABOADA, “2009 Progress report on RERTR activities in Argentina”, *Proceedings of the 2009 RERTR Meeting*, Beijing, China, Nov. 1-5, 2009.
- [2] IPEN, 2009. <https://www.ipen.br/sitio/?idc=5844>
- [3] A. J. BAKEL, D. C. STEPINSKI, A. GUELIS, A. HEBDEN, A. LEYVA, L. HAFENRICHTER, P. GENTNE, G. F. VANDEGRIFT, “Progress in technology development for conversion of ⁹⁹Mo production from HEU targets-development of new separation schemes, and new processing equipment”, *Proceedings of the 2006 RERTR Meeting*, Cape Town, South Africa, Oct. 23-Nov. 2, 2006.
- [4] DADACHOVA, K.; LA RIVIERE, K.; ANDERSON, P. Improved processes of molybdenum-99 production. *J. Radioanal. Nucl. Chem.*, v. 240, p. 935-938, 1999.
- [5] R.A. LEONARD, L. CHEN, C.J. MERTZ, G.F. VANDEGRIFT, “Progress in dissolving modified LEU cintichem targets”, *Proceedings of the 1996 RERTR Meeting*, Seoul, Korea, Oct. 7-10, 1996,.

[6] D. WU, S. LANDSBERGER, G. F. VANDERGRIFT, “Progress in chemical treatment of LEU targets by the modified cintichem process”, *Proceedings of the 1996 RERTR Meeting*, Seoul, Korea, Oct. 7-10, 1996.

[7] M.A. OLAZABAL, M.M. ORIVE, L.A. FERNANDEZ, J.M. MADARIAGA, “Selective extraction of vanadium (V) from solutions containing molybdenum (VI) by ammonium salts dissolved in toluene”, *Solv. Extr. Ion Exch.*, v. 10 (4), p. 623–635, 1992, **apud** L. ZENG, C. Y. CHENG, “A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts Part II: Separation and purification”, *Hydrometallurgy*, v. 98, p. 10-20, 2009.

[8] S.K. TANGRI, A.K. SURI, C.K. GUPTA, “Development of solvent extraction processes for production of high purity oxides of molybdenum, tungsten and vanadium”, *Trans. Indn Inst. Met.*, v. 51 (1), p. 27–39, 1998, **apud** L. ZENG, C. Y. CHENG, “A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts Part II: Separation and purification”, *Hydrometallurgy*, v. 98, p. 10-20, 2009.

[9] A. Bakel, A. Leyva, T. Wiencek, A. Hebden, K. Quigley, J. Falkenberg, L. Hafenrichter, G. Vandegrift, “Overview of process related to implementation of the LEU-Modified cintichem process”, *Proceedings of the 2008 RERTR Meeting*, Washington, D.C. USA, Oct 5-9, 2008.