# DISSOLUTION AND ION EXCHANGE OPERATIONS MATHEMATICAL MODELING IN A $^{99}$MO PRODUCTION PROCESS FOR MEDICAL PURPOSES

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# DISSOLUTION AND ION EXCHANGE OPERATIONS MATHEMATICAL MODELING IN A $^{99}$MO PRODUCTION PROCESS FOR MEDICAL PURPOSES

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This work deals with the mathematical modeling of target dissolution and AG1X8 ion exchange column in the process employed to obtain $^{99}$Mo from irradiated LEU (low enrichment uranium) targets.

Parameters describing temperature influence on reaction rate and the order of cladding dissolution reaction were determined. In order to obtain the parameters needed to modeling the breakthrough and elution curves of AG1X8 purification column, adsorption equilibrium isotherms were studied in molybdenum concentration range from 1 mg/L to 10 g/L in alkaline media at room temperature, 40 ºC and 60 ºC. Langmuir and Freundlich models were used to fit adsorption isotherms data and numerical optimization was applied to calculate mass transfer coefficients, needed to solve the partial differential equations describing the column loading and elution steps.

## INTRODUCTION

Molybdenum-99 is employed to obtain Tc-99m generators for medical purposes, based on the radioactive decay:

$$^{99}\text{Mo} \xrightarrow[66\,\text{h}]{\beta^-} {}^{99\text{m}}\text{Tc}$$
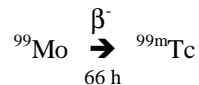
Molybdenum occurs in nature having the following isotopic composition: 15,86% $^{92}$Mo, 9,12% $^{94}$Mo, 15,70% $^{95}$Mo, 16,50% $^{96}$Mo, 9,45% $^{97}$Mo, 23,75% $^{98}$Mo and 9,62% $^{100}$Mo. The two most important ways to obtain $^{99}$Mo nuclide are the neutron capture of $^{98}$Mo and the $^{235}$U fission, the latter giving the best $^{99}$Mo yield.

The technology for producing $^{99}$Mo from the $^{235}$U irradiation is well known for the high-enriched uranium targets (HEU). However, since 1992, IAEA (International Atomic Energy Agency) has restricted the use of HEU fuels, and studies have been developed to replace them for low enriched (LEU) fuels and targets. The choice of the new target must take into account the $^{99}$Mo yield the target fabrication process and avoid introducing many changes in the well-known HEU process to obtain $^{99}$Mo.

For our first studies, uranium silicide targets has been used due to its high density, which allows the required $^{99}$Mo yield, by keeping the same geometry of HEU targets. The main steps of the molybdenum treatment, based on the process proposed by Sameh et al. [1] are:

- irradiation of uranium silicide targets,
- alkaline dissolution of irradiated targets,
- ion exchange operation for obtaining $^{99}$Mo with the required chemical and radiochemical purity and

- uranium recovery and waste treatment.

The mathematical simulation of the unit operations in a radioactive chemical process is important to minimize the radioactive material handling, and to allow greater process flexibility. In this work, parameters concerning target dissolution reactions and ion exchange columns are studied, in order to obtain the mathematical models describing these operations.

## TARGET DISSOLUTION

Chemical processing of irradiated LEU material begins with uranium silicide targets dissolution. Firstly, aluminum cladding of Al-$U_3Si_2$ slabs is dissolved, followed by the attack of $U_3Si_2$ by a KOH solution.

Aluminum dissolution in alkaline media is obtained by the following reaction:

$$Al + KOH + H_2O \rightarrow KAlO_2 + 3/2\ H_2$$
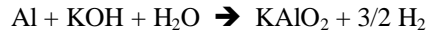
The studies of the temperature effect on the dissolution rate has showed an Ahrenius type relation (Figure 1):

$$r\ \alpha\ exp.(-E_a/RT)$$

where,

$r$  => reaction rate (mol/$cm^2$.s)
$E_a$ => activation energy (kJ/mol)
$R$ => perfect gas constant (8,314 J.$mol^{-1}$.$K^{-1}$)
$T$ => temperature (K)

being,

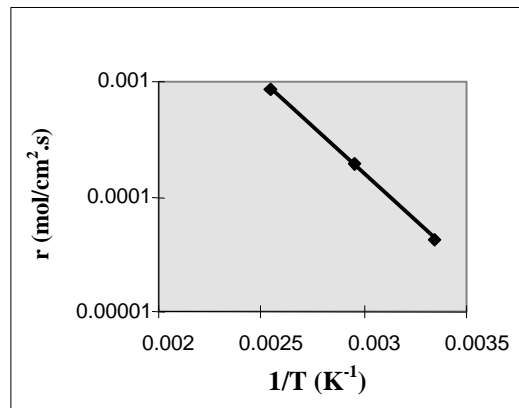$$r = 11,514\ exp.(-3732,2/T) \tag{1}$$

and

$E_a = 31,029$ kJ/mol



Figure 1. Reaction Rate as a Function of Temperature

The reaction order was also evaluated. The relationship between the reaction rate and the KOH concentration can be described by the equation:

$$r = \frac{k_1[KOH]}{1 + k_2[KOH]} \qquad (2)$$

where,

$k_1$ = 0,0162 mol$^{-1}$.L
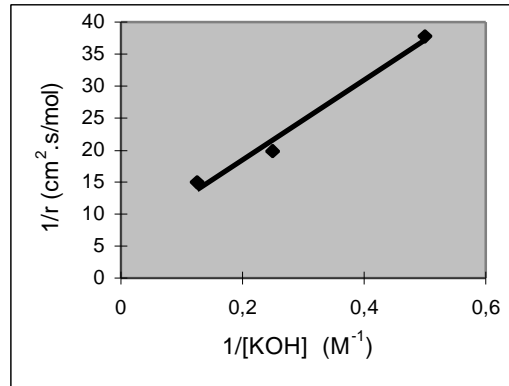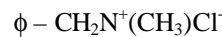$k_2$ = 0,101 mol$^{-1}$.L



Figure 2: Dissolution Rate as a Function of KOH Concentration at 120 ºC

## ION EXCHANGE COLUMNS

In the first step of molybdenum-99 purification, the solution issued from the alkaline dissolution is passed through a column filled with the AG1X8 resin, which retains molybdenum quantitatively. This resin can be schematized as:

$$\phi - CH_2N^+(CH_3)Cl^-$$

After a preliminary treatment [2], the resin goes to the form OH$^-$:

$$R\text{-}Cl + OH^- \Leftrightarrow R\text{-}OH + Cl^-$$

The silicide targets are not yet available for irradiation, so the experiments were carried out by using simulated solutions, which were obtained by the MoO$_3$ dissolution in KOH media by adding a $^{99}$Mo tracer. MoO$_3$ is acid and its dissolution gives a series of anions like Mo$_2$O$_7^{2-}$, Mo$_7$O$_{24}^{6-}$ and others. Nevertheless, in a strong alkaline medium, the only species present is MoO$_4^{2-}$, which is retained in an AG1X8 resin by the reaction:

$$2\,R\text{-}OH + Mo_2O_4^{2-} \Leftrightarrow R_2MoO_4 + 2\,OH^-.$$
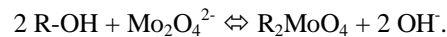
## BATCH EXPERIMENTS

Batch experiments were accomplished in order to:

- verify the equilibrium contact time,
- study the distribution coefficients and the retention percentage of Mo$_2$O$_4^{2-}$ in AG1X8 resin, in KOH, HNO$_3$ and HNO$_3$-NaNO$_3$ media and their dependence on media concentration and temperature,
- obtain the equilibrium isotherms of molybdenum under these conditions.

The analytical control was made by gamma spectrometry by means of the 140 KeV peak of $^{99}$Mo-$^{99m}$Tc pair in a scintillation detector.

The results for the distribution coefficients and % of retention are described by Yamaura et al. [2]. These parameters increase as the temperature rises and decrease with the KOH concentration increasing. Similarly, the retention in $HNO_3$ medium is enhanced by the temperature increase and decreases when $HNO_3$ concentration rises. The comparison between the % retention in $HNO_3$ and KOH media has shown a better retention in KOH medium. The equilibrium contact time is 15 minutes, so this time was adopted for the batch experiments.

## EQUILIBRIUM CONSTANTS

The first step for modeling the breakthrough and elution curves is to determine the adsorption equilibrium constants of the ion in the resin. In order to obtain these parameters, 50 mg of dry resin were contacted with molybdenum solutions in the concentration range 0,001 g/L to 10 g/L in KOH media 0,01, 0,1, 0,5, 1,0, 2,0 and 3,0 N at the temperatures 20 ºC, 40 ºC and 60 ºC.

The most important conclusions of these studies were:

- the relation between the molybdenum concentration in resin and the molybdenum concentration in feed is linear,

- for the molybdenum concentrations in feed below 0,5 g/L, the equilibrium isotherms are linear and the slopes of the curves at 60 ºC are 1,8945, 0,0982 and 0,0638 for KOH concentrations 0,01N, 1,0N and 2,0 N, respectively.

- Langmuir model can be adopted to describe the obtained equilibrium isotherms when Mo concentrations in feed are below 7,5 g/L.

**Langmuir model**:

$$m = \frac{K_1 K_2 c}{1 + K_2 c}$$ (3)

where:

$m$ => adsorbed material mass/adsorbent material mass

$c$ => ion concentration in solution

$K_1, K_2$ => constants

Table 1 shows $K_1$ and $K_2$ calculated constants at 40 ºC.

Table 1: Langmuir Constants for Molybdenum at 40 ºC

| [KOH] (N) | $K_1$ (mg/mg) | $K_2$ (mL/mg) |
|-----------|---------------|---------------|
| 0,5 | 0,052 | 3,50 |
| 1,0 | 0,083 | 2,25 |
| 2,0 | 0,10 | 1,12 |
| 3,0 | 0,14 | 1,17 |

- Freundlich isotherm model can be adopted to describe the results for the systems being feed concentrations below 3,0 g/L.

**Freundlich model**:

$$m = Kc^{1/n}$$ (4)

where:

*m* => adsorbed material mass/adsorbent material mass

*K, n* => constants
*K* and *n* constants calculated values could be observed in Table 2.

Table 2: Freundlich Constants for Molybdenum at 40 ºC

| [KOH] (N) | K | n |
|-----------|------|------|
| 0,5 | 0,70 | 1,43 |
| 1,0 | 0,73 | 1,37 |
| 2,0 | 0,78 | 1,29 |
| 3,0 | 0,85 | 1,17 |

the adsorption in resin decreases as the temperature increases (Figure 3).
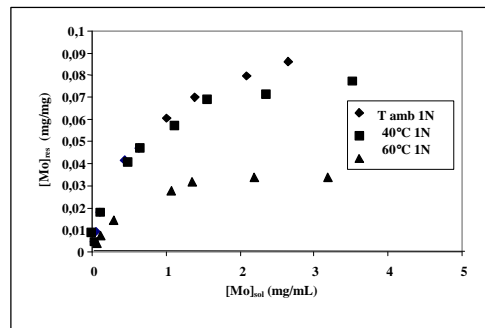


Figure 3. Equilibrium Isotherms in KOH Media

**COLUMN EXPERIMENTS**

For modeling loading, washing and elution steps in the column, the following assumptions were adopted: tubular reactor, spherical particles and constant physical and geometrical bed features.

In the loading step, the curves representing ion concentrations as a function of time, effluent volume, mole or equivalent numbers are called breakthrough curves. In a real adsorption, mass transfer velocity is finite, so the ion is not instantly adsorbed in the resin. The slope of the breakthrough curve is given by the adsorption rate, greater is the adsorption, and more vertical the curve will be [3].

Adsorption zone can be defined as an extension of bed in which the concentration changes from the concentration at the liquid phase inlet to the resin saturation concentration. When the fluid is introduced at the first time in the bed, the adsorption zone is formed and flows through the bed until it arises in the bed outlet like the breakthrough curve. Some parameters concerning the adsorption zone can be related by:

$$F = \frac{z - fz_a}{z}$$

where:

*F* => fraction of the bed which is not saturated.

*z* => distance from a point in the bed to the bed inlet

$z_a$ => adsorption zone width

$f$ => fraction of the maximal capacity in the adsorption zone which is not saturated

The adsorption zone width can also be related to the number of transfer units $N_{Ol}$ and to the transfer unit height $H_{Ol}$ by the equation [3]:

$$z_a = N_{Ol}.H_{Ol} \tag{5}$$

being $H_{Ol} = v/k_l a$, where $v$ is the liquid velocity in the bed, $a$ is the specific superficial area and $k_l$ the mass transfer coefficient. Undimensional relations can estimate the latter and it is an important parameter for the modeling of ion exchange columns.

To describe the breakthrough curve, the following expression based on the molybdate ion balance in the liquid phase was adopted, without take into account the axial dispersion:

$$\frac{\partial X}{\partial t} = -v\frac{\partial X}{\partial z} + \frac{k_l a}{e}( X - X^*) \tag{6}$$

with the initial condition:

$X = X_{inicial}$    for $t = 0$    $0 \pounds z \pounds Z$

and the boundary condition:

$X = X_{alim}$  for $t > 0$     $z = 0$

being $z$ the distance from the considered point until the bed inlet, $e$ the bed porosity and $t$ the feed time, $X$ is the molybdenum concentration in the liquid phase and $X^*$ the molybdenum concentration at equilibrium.

For the elution curve modeling, the tubular reactor assumption was retained, but taking into account the axial dispersion, the adsorption coefficient $K_{ad}$ and the desorption coefficient $K_{de}$ of molybdate ion in resin [5]. $K_{ad}$ and $K_{de}$ constants are related to the equilibrium parameters by the following equation:

$$K_2 = K_{ad}/K_{de} \tag{7}$$

where $K_{de}$ is the Langmuir constant. The desorption terms depend on the adsorbed concentration of the ion in the column, and the desorption coefficient $K_{de}$ is a function of ion concentration in liquid phase and of the empty positions in the bed ($q_{máx} - q$).

After loading and washing steps, the ion concentration in the column is greater than the maximal concentration allowed by the equilibrium conditions [5]. So, at the beginning of elution step, only the desorption term is present, and the kinetic law is expressed by:

If $q(t) > q_{máx}$

$$\frac{\partial q}{\partial t} = -K_{de}q(t) \tag{8}$$

The global balance in the solid phase is:

$$h\frac{\partial q}{\partial t} = \int_0^h \{K_{ad}c(z,t)[q_{max} - q(t)]K_{de}q(t)\}dz \tag{9}$$

being $h$ the bed height.

The mass differential balance in the liquid phase is given by:

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}+\frac{1-e}{e}\{K_{ad}c[q_{max}-q(t)]-K_{de}q(t)\}=D_a\frac{\partial^2 c}{\partial^2 z^2} \qquad (10)$$

being $D_a$ the axial dispersion coefficient.

with the boundary layers:

If $z = 0$,

$$D_a\frac{\P c}{\P z}=-v[c_{feed}-c]$$

If $z = h$,

$$D_a\frac{\P c}{\P z}=0$$

and the initial conditions:

$c(0, t) = c_{feed}$

$c(z,0) = 0$

$q(0) = q_e$

being $q_e$ the ion concentration in resin after the loading and washing steps.

## EXPERIMENTAL RUNS

A jacketed glass column 4 mm ID, filled with AG1X8 resin was used for the loading, washing and elution steps.

The loading was carried out at 40 ºC, with 28 ml of a 5,0 g/L molybdenum solution in 3 N KOH medium, with a flow rate of 112,5 mL/h, after that, 25 mL of 3 N KOH was percolled in the column for the washing step. For the elution step, 25 mL of HNO$_3$ 3 N were used, at the same flow rate of the loading step.

The physicochemical features of the resin and the geometric parameters of the bed are showed in Table 3. Fractions of 1 ml were collected at the column outlet and the samples were analyzed by gamma spectrometry to evaluate the molybdenum concentration variation as a function of effluent volume.

Table 3. Resin Properties and Bed Characteristics

| | |
|---|---|
| Bead radius | 0,2655 mm |
| Bed inside diameter | 4 mm |
| Bed height | 15,2 cm |
| Void fraction | 0,45 |
| Bed density | 0,44 g/cm$^3$ dry bed |
| Specific superficial area | 101,7 cm$^2$/cm$^3$ |
| Exchange capacity | 3,2 meq/g dry resin |

## RESULTS AND DISCUSSION

For the study of the breakthrough curve, the column was divided in several equal segments. In order to solve the system of partial differential equations, the spatial derivative was discretized, so the resulting system of ordinary differential equations could be solved by a Runge-Kutta method, by means of an algorithm presented by Ebert et al.[6]. The mass transfer coefficient $k_l$ was calculated by using equation (6), following the procedure described by Gonçalves et al. [7].

The resolution of the system describing the elution curve was also achieved by discretizing the spatial variable and solving the ordinary differential equations system by the same algorithm of the loading step. In the elution curve case, $K_{ad}$ and $K_{de}$ were evaluated by numerical optimization, by using the Flexiplex algorithm, which is based on the Nelder-Mead flexible tolerance method [8]. Calculated parameters for the elution curve are shown in Table 4.

Table 4. Calculated Parameters

| | |
|---|---|
| $k_l a$ | 0,066 s$^{-1}$ |
| $K_{ad}$ | 0,002 cm3.g$^{-1}$.s$^{-1}$ |
| $K_{de}$ | 0,00043 s$^{-1}$ |
| $D_a$ | 0,088 m$^2$.s$^{-1}$ |

By introducing the calculated parameters in Equations, respectively, the fitting between experimental and proposed model points for the breakthrough and elution curves, respectively are obtained and can be seen in Figures 4 and 5.
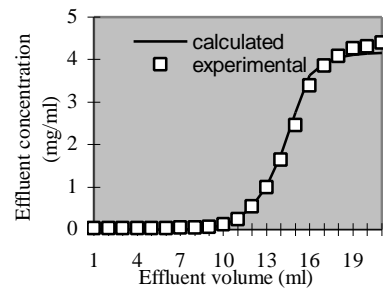


Figure 4. Calculated and Experimental Breakthrough Curves for Molybdenum in
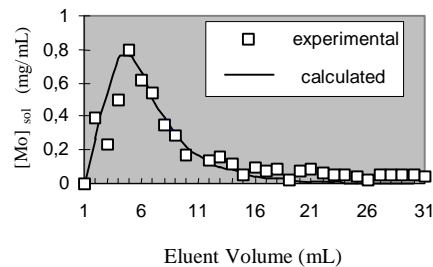AG1X8 resin at 40 ºC in 3 N KOH Medium



Figure 5. Calculated and Experimental Elution Curves for Molybdenum in
AG1X8 resin at 40 ºC in 3 N HNO$_3$ Medium

## CONCLUSION

The adsorption behavior of molybdenum in ion exchange columns filled with AG1X8 resin was studied. Equilibrium adsorption constants were determined and breakthrough and elution curves were mathematically interpreted. The obtained fitting between experimental and proposed model points have showed their adequacy for ion exchange systems.

The same equations can be applied for others ion exchange columns breakthrough and elution curves on the purification molybdenum process, since the equilibrium constants have been previously determined.

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