Recovery of Molybdenum using Alumina Microspheres and Precipitation with Selective Organic Reagents

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Presented at the 1998 International Meeting on
Reduced Enrichment for Research and Test Reactors

October 18 - 23, 1998

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ABSTRACT

In this paper is presented a study for the optimization of dissolution of the UAl_x plates used for irradiation and production of radiomolybdenum. The alloy is dissolved in nitric acid with mercury as catalyst. The separation and concentration of the molybdenum was achieved using a chromatographic grade alumina microspheres column. The purified eluted molybdenum is finally precipitated using one of the selective reagents: alizarine blue, α,α'-bypiridine and 1,10-phenanthroline. Any one of the obtained precipitate can be fired to the molybdenum trioxide. The interference of the following elements was studied: Re(VII), U(VI), Cr(VI), W(VI), V(V), Te(IV), Ti(IV), Zr(IV), Th(IV), Fe(III), Au(III),Ru(III), Al(III), Bi(III), Sb(III), Ce(IV),Pr(III), Sc(III),Y(III), Sm(III), Ba(II), Sr(II), Ni(II), Co(II), Cs(I). The molybdenum precipitates were characterized by gravimetric, CHN, TG, DTG, IR and X-ray diffraction analyses.

INTRODUCTION

The target to be irradiated in the IEA-R1 reactor for the molybdenum production is an aluminum cladded uranium-aluminum alloy with the approximate composition of UAl_3. Six plates with 17g of aluminum and 1g of uranium are irradiated in each process.

The most used methods for the target dissolution use an alkaline medium. Lewis[1] and Ali[2] employ an alkaline digestion with 3-6M NaOH. The main constituents of the plate are dissolved, namely aluminum and some fission products such as alkaline and alkaline earth metals, antimony, tin, iodine, tellurium and molybdenum. Then the suspension is filtered to remove the insoluble products, including the uranium. Aluminum and molybdenum are collected in the filtrate. Further molybdenum purification is made in a column of strong anionic ion exchanger, which absorbs molybdenum quantitatively together a significant part of fission products.

If the choice for the target dissolution is an acid it must be done a careful evaluation to select the suitable acid. Hydrochloric acid dissolves the aluminum but leads to anionic uranium complexes such as $UO_2Cl_3^-$ and $UO_2Cl_4^{2-}$. Sulfuric acid also dissolves the aluminum but contributes to the formation of anionic complexes, such as $UO_2(SO_4)_3^{4-}$. On the other side, to avoid the corrosion of the equipment, in general built with stainless steel, only nitric acid is an acceptable dissolution agent [3]. But, in this medium the aluminum dissolution is normally inhibited. This known passivity can be avoided by addition of a small amount of mercury. There are some studies of aluminum dissolution with nitric acid catalyzed by Hg(II) nitrate in which the aluminum nitrate [4] was obtained for different geometric forms of an U-Al alloy, plate, cylinder and parings[5-7].

In the present paper it is discussed the optimization of the acid catalyzed dissolution of the Al-U target followed by the separation and concentration of the molybdenum onto an chromatographic grade alumina microspheres column. The purified eluted molybdenum is finally precipitated using one of the selective reagents: alizarine blue, α,α'-dipyridine and 1,10-phenanthroline. Any one of the precipitate can be fired to the molybdenum trioxide.

EXPERIMENTAL

Aluminum Dissolution Chemistry

The dissolution of aluminum with nitric acid without mercury as catalyst is very slow due the formation of an adherent oxide film on the metallic surface. The dissolution is improved by the presence of mercury as catalyst which promote the attack in three successive steps: (a) the reduction of Hg(II) ion to a metallic mercury; (b) formation of an aluminum amalgam; and (c) the dissolution of the amalgam by the nitric acid.

The study was made using aluminum 1060 plates, with 102g each one, into a pyrex reactor. The dissolution was monitored via analysis of the aluminum by precipitation with 8-hydroxiquinoline[8,9] and the determination of the free acid by potentiometric method using potassium oxalate to complex the aluminum ion[10]

For the aluminum dissolution two process was developed: (a) the immersion of the plates into nitric acid and (b) the continuous addition of nitric acid to the aluminum plates.

In the procedure (a) the dissolution time was studied with the change of HNO_3concentration (Table I), and with the catalyst concentration (Table II).

Table I- Time of dissolution with the HNO_3 concentration

$[HNO_3]$ (M)	Time (min.)
2,0	**280**
4,0	**230**
6,0	**180**
8,0	**250**
14,0	**270**

Table II. – Dissolution time with Hg(II) concentration

[Hg(II)](M)	Time (h)
$7{,}4.10^{-4}$	**22**
$1{,}1.10^{-3}$	**8**
$1{,}8.10^{-3}$	**3**
$3{,}0.10^{-3}$	**3**

For the procedure (a) the best concentration of nitric acid was in the 4-6M range and the Hg(II) concentration was $1.8.10^{-3}$M

In procedure (b) the volume of nitric acid used was 2.5l for each experiment with the concentration of nitric acid and Hg(II) indicated by (a). In these steps are studied the acid concentration of the solution of dissolution with the time(Table III)

TableIII- Acid concentration of solution (M) with the time of dissolution

Time (min.)	$[H^+]$(M)
30	**0,36 (acid deficient)**
60	**0,75**
90	**0,05**
120	**0,35**
150	**0,13 (acid deficient)**
180	**0,17**

The results of the experiments worked out in both process allowed to conclude for the choice of the continuous addition of nitric acid to aluminum plates. In this procedure a violent reaction does not occur as in immersion process. The temperature is easily controlled to 50-80°C range. In all the experiments the reaction started 2 to 6 minutes after the contact of the acid with the aluminum plate.

Since the mass of uranium in the target is only approximately 6% of the aluminum mass, the control of the reaction is made via dissolution of the aluminum. Uranium is dissolved by the oxidation with nitric acid and is solubilized as uranyl nitrate.

The final solution has a concentration of 0.1 to 0.2M in HNO_3, which is the recommended acid concentration for loading the molybdenum onto the alumina column. The optimized process uses initial 6M HNO_3 and $1.8.10^{-3}$M Hg as catalyst. One plate can be totally solubilized in 180 minutes.

Chromatographic Separation of Molybdenum Onto Alumina Column

The behavior of minor amount of molybdenum(VI) in the presence of large quantity of aluminum nitrate and separation of Mo(VI) from Al(III) was studied with the aid of a chromatographic process using an alumina column. The separation of both elements is in favor of the selective uptake of molybdenum by the alumina. The solution containing both elements is an acidified aluminum nitrate of high concentration in aluminum and was percolated through a bed of specially synthesized alumina microspheres.

Unfortunately, alumina is usually supplied as a powder. Although it can be used as small column, for preparative operation or work with greater volumes, powder alumina is not reliable, and does not perform well.

In this work a new type of chromatographic alumina was used specially prepared as microspheres. This material fitted well as the bed for chromatographic columns. The alumina microspheres have been prepared by the sol-gel process, based on references[11,12]. This type of alumina exhibited an excellent performance as chromatographic material. For the present work it was used alumina with microspheres diameter ranging from 0.50 to 0.80 mm.

Molybdenum uptake by alumina microspheres

For ion exchange experiments was employed a chromatographic column with 3g alumina microspheres in the bed column. Determination of adsorption/desorption characteristics of this substrate for molybdenum was carried out under dynamic conditions. Glass columns were 8 mm in diameter and the volume of microspheres was 3.5 ml. After filling, the column was washed with 200 ml 1M HNO_3, 100 ml distillated water, 100 ml 1M NH_4OH and finally 200 ml H_2O. The column was conditioned with 200 ml 1M HNO_3. The adsorption and desorption velocities were maintained between 1 and 3 $ml.min.^{-1}cm^{-2}$.

Molybdenum was assayed by hanging mercury dropping electrode voltametric technique, with tartaric acid as electrolytic support. The electrolytical cell has a saturated calomel electrode as reference. The auxiliary electrode was a platinum wire.

Figure 1 depicts the adsorption of Mo(VI) as a function of acidity of the influent solution. Optimal adsorption was attained at 0.1-0.2M HNO_3.

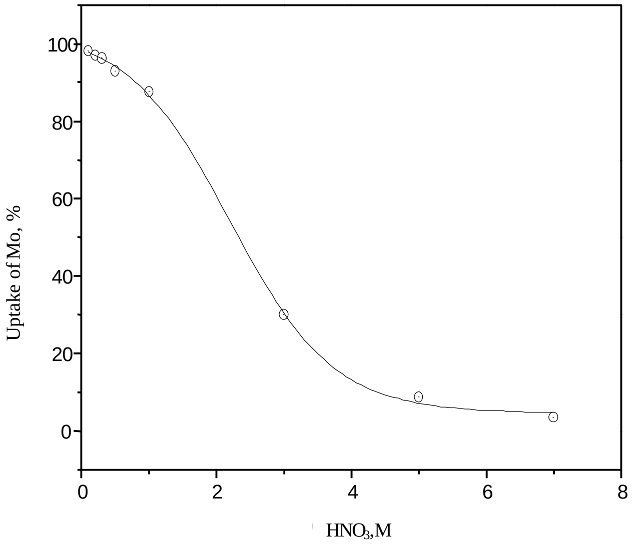

Fig.1 – Uptake of molybdenum by alumina microspheres as function of nitric acid concentration

Desorption of molybdenum from alumina microspheres

The desorption of molybdenum was carried out after washing the column with 0.1M HNO_3 and distilled water. Molybdenum was then eluted with 1M NH_4OH. The elution volume was 100 ml.

Figure 2 depicts the results of the desorption of molybdenum from the alumina column. As observed from this figure the desorption of molybdenum is better with NH_4OH greater than 1M.

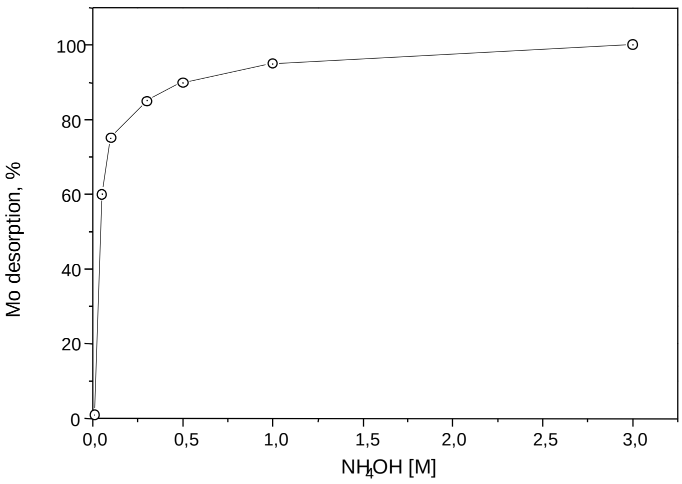

Figure 2 – Desorption of molybdenum from the alumina column as function of ammonium hydroxide concentration

In this work it was also searched the optimal volume of ammonium hydroxide solution for the desorption of molybdenum and the temperature influence on adsorption and desorption of molybdenum as well. Figures 3 and 4 depict the results of both parameters.

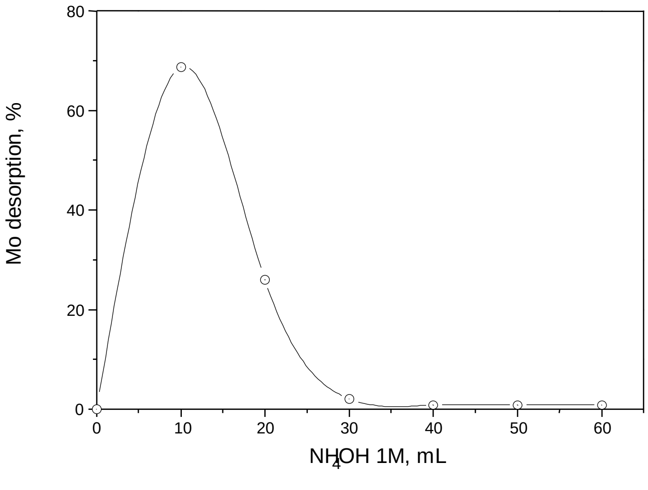

Fig.3 – Molybdenum elution as function of 1M NH_4OH volume

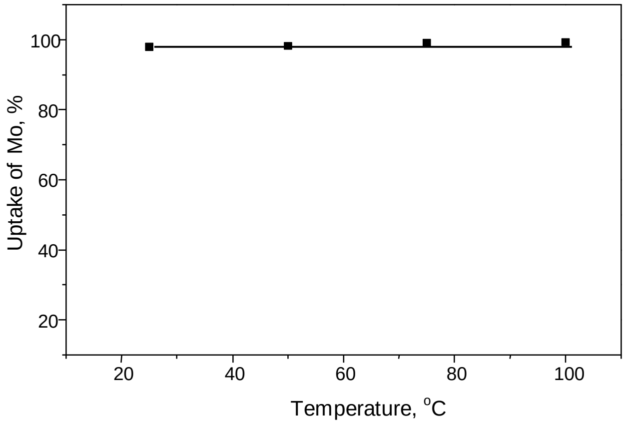

Fig. 4 – Molybdenum uptake as function of the loading solution temperature

Summarizing it was concluded that molybdenum solution was better purified, and decontaminated from aluminum, when it was adsorbed onto alumina microspheres from a 0.1M HNO_3 solution and, after washing the column with water, it was eluted with 1M NH_4OH at 25°C.

Selective Precipitation Reactions for Molybdenum

The eluted molybdenum was selectively precipitated with the specific reagents α,α'-dipyridine, 1,10-phenanthroline and alizarin blue, whose application as selective reagents for the precipitation of molybdenum was introduced by the authors for the first time.

The precipitation of molybdenum using alizarin blue (7,8-dihydroxy-5,6-phtalquinoline) is a novel reaction. The precipitate formed in acidic medium is crystalline and has a violet color. Only copper(II) forms a precipitate in the same conditions, but it can be differentiated by its color. The alizarin blue copper(II) precipitate is blue, while the precipitate formed with molybdenum and alizarin blue is violet.

The reaction is very sensitive. Using three or more micrograms of molybdenum(VI) the precipitation occurs immediately. For smaller mass of molybdenum the precipitate appears after a few minutes. With this novel reaction it is possible to identify 0.1 microgram Mo. Molybdenum is not precipitated from an alkaline medium.

The following ions do not precipitate with alizarin blue from hydrochloric acid: Re(VII), U(VI), Cr(VI), W(VI), V(V), Te(IV), Ti(IV), Zr(IV), Th(IV), Fe(III), Au(III), Al(III), Bi(III), Sb(III), Pr(III), Sc(III), Ba(II), Sr(II) and Ni(II). The ions Co(II), Ni(II) and Zr(IV) develop blue solutions, while Sb(III), Te(IV), Pr(III), Ba(II), Sr(II), Sc(III) and Fe(III), exhibited reddish color in hydrochloric acid.

This novel precipitation reaction will be explored in analytical chemistry for the separation and identification of molybdenum.

The precipitation of Mo(VI) with α,α'-dipyridine and 1,10-phenanthroline is also selective. The precipitation was used for the separation of molybdenum mainly from ruthenium, tellurium and iodine. The precipitation of Mo(VI) was done at pH 3.0. The precipitate was washed out with a solution of HCl of pH 3.0 and rinsed with distilled water and finally with ethyl alcohol. The precipitate is white and volumous. For both organic reagents the following ions do not interfere, not being precipitated: Cs(I), Ba(II), Sr(II), Zn(II), Al(III), Dy(III), Fe(III), La(III), Nd(III), Pr(III),Sm(III), Y(III), Ce(IV), Ru(III), Te(IV) and U(VI). The unique ion precipitated is Sb(III), but its precipitation occurs only at less acidic solution. An analysis by X-ray fluoresce confirmed the absence of above mentioned elements in the precipitate.

Both precipitates were characterized by gravimetric, CHN , TG, DTG, IR and X-ray diffraction analyses. The following stoichiometry was assigned: $MoO_3.C_{12}H_8N_2.H_2O$ and $MoO_3.C_{10}H_8N_2$ for α,α'-bypiridine and 1,10-phenanthroline, respectively.

The precipitates obtained using the three reagents here mentioned can be fired to MoO3.

In this work, emphasis was given to the study for the Mo(VI) separation from ruthenium, tellurium and iodine, that as anionic complexes are adsorbed onto the alumina bed and then eluted from the alumina together with molybdenum.

These novel precipitations reaction will be explored in analytical chemistry for the separation and identification of molybdenum.

CONCLUSION

The dissolution process optimization with nitric acid and mercury as catalyst was performed and the best results are 2.5 l of 6M HNO_3 and $1.8.10^{-3}$M Hg(II) as the best parameters.

The initial separation of molybdenum by sorption/desorption onto alumina microspheres specially synthesized for this purpose was successfully done. This step eliminates the most probable impurities as Cs(I), Ba(II), Sr(II), Zn(II), Al(III), Dy(III), Fe(III), La(III), Nd(III), Pr(III),Sm(III), Y(III), Ce(IV) and U(VI).

The eluted molybdenum, containing iodine, tellurium and ruthenium, was selectively precipitated with the specific reagents: alizarin blue, α,α'-dipyridine and 1,10-phenanthroline, whose application as selective reagents for the precipitation of Mo(VI) gave a pure molybdenum oxide

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