



Journal of Applied Sciences

ISSN 1812-5654

science
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Separation of Molybdenum-Uranium by a Process Combining Ion Exchange Resin and Membranes

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Abstract: The purpose of this study is to determine whether the electrodeionization with ion-exchange resin is suitable for removing uranium from a solution containing molybdenum. A hybrid process combining ion exchange (resins and membranes) using electric current. For this electroextraction process, the cation exchange resin is introduced into an electrodialysis cell and compressed between two cations exchange membranes. We have investigated a continuous electroextraction process. As important result we note that: The factor of selectivity, r , for molybdenum versus uranium is superior to 3; the concentration in radio active element (U_3O_8) is lower than 1.5 mg L^{-1} and small cell voltage is observed.

Key words: Electroextraction, Ion-exchange resin membrane

INTRODUCTION

For the removal of ions from low concentration solutions, conventional ion-exchange is preferred (Strathmann, 1988). However, ion exchange is a discontinuous process, which requires chemical regeneration cycles providing consequential effluents. In our previous studies (Basta *et al.*, 1998). It has achieved the electroextraction of Pb^{2+} with cation exchange textiles. This same process has been used for the water demineralization (Dejean *et al.*, 1998). The electroextraction have been used also to remove impurities from phosphoric acid. A ratio close to 30% were obtained for some elements (Ben Chehida, 2006). With this hybrid method Dzyazko (2006) demonstrated the possibility to purify solutions containing Ni^{2+} ions Smara *et al.* (2005) show that the electrodeionization of heavy metals (Pb^{2+} and Cd^{2+}) from diluted solutions gives some interesting results in terms of efficiency of purification.

For desalination of dilute solutions, a number of methods have been proposed in order to tackle the increasing ohmic resistance and the polarization phenomenon (Oren *et al.*, 2002). The aim of the present study is to search the possibilities to remove the molybdenum existing with uranium in the solution after the liquid-liquid extraction of uranium from the leach solution of uranium ore. In our case we used a hybrid process combining exchange membrane-resin and electric

current. The solution flows continuously through the cation exchange resin which is introduced into an electrodialysis cell and compressed between two cations exchange membranes. After having fixed the current densities, we studied the molybdenum recovery from hydrochloric acid solution containing 40 mg L^{-1} of molybdenum and 20 mg L^{-1} of uranium.

This theme of research which concerns the purification of the leach solutions of the uranium ores by the membrane process has been investigated since 1998 in the laboratory of analysis (Nuclear Research Center of Draria). We notice that few scientific investigations can be found in this field. The first results have been presented during the second symposium integration of membranes in processes (Lounis and Gavach, 2003).

MATERIALS AND METHODS

Ion exchangers: The ion-exchange membranes are commercial electrodialysis membranes, Ar 108 CZP 401 and CR61 CZL 336, manufactured by Ionics Corporation. Their characteristics are given in Table 1. The cation-exchange resin is DOWEX 50 X 8 BDH.

Figure 1 is a schematic representation of the laboratory cell used in this study. The solution flows in the central compartment between two cation-exchange membranes (CR61 CZL). On both sides of the central compartment, two concentration compartments receive the cations species. The 10^{-1} M NaCl solution flowing in

Table 1: Ions exchange membranes properties

Type	AR204 UZL	CR61CZL
Thickness (mm)	0.57	0.50
Exchange capacity (Meq g ⁻¹)	1.9	2.7
Specific resistance (Ω cm ²) in 0.5 M NaCl	9-11	8-11
Water content (%)	30	33

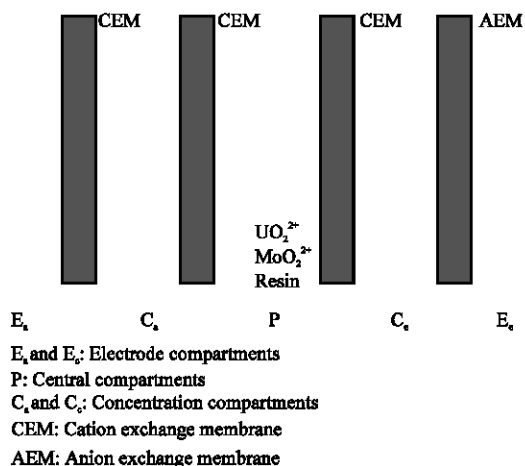


Fig. 1: Electrodialysis cell schematic

the electrode compartment prevents a composition modification of the concentration sides, which could be caused by electrode reactions. The different elements of the cell are made of plexiglas and are separated by interposed membranes between silicone and viton gaskets. The electrodes are platinum-coated titanium sheets. The effective area of each membrane and of each electrode is 40 cm². The distance between the membranes is 4 mm. The concentration and the electrode solution flows are obtained by a four-head Watson-Marlow 503S peristaltic pump giving a solution flow up to 4.5 L h⁻¹. The current intensity is supplied by a Lambda LQ534W current generator.

Operating conditions: In order to fix the current density, electrodialysis over 2 h was investigated. To avoid the polarization phenomenon we used a leach liquor (Lounis and Gavach, 1997).

We studied the continuous electroextraction process. The resin and cation exchange membranes were in H⁺ and Na⁺ form. The solution containing 40 mg L⁻¹ of molybdenum and 23.6 mg L⁻¹ of uranium in chlorhydric acid medium was circulated in the feed compartment with varied flow rates 0.06, 0.12 and 0.18 L h⁻¹ corresponding to a circulation rate 0.0926 cm s⁻¹ to 0.277 cm sec⁻¹, respectively. An acidic (HCL) and a saline (NaCl) solution was circulated in C_a, C_c and E compartments. In all experiments the electrode compartment contained 1 L. Provided the previous studies results (Basta *et al.*, 1998), the current intensity is maintained at 100 mA. Uranium

was titrated with a calorimetric titration using Arsenazo III as complexing agent (Savin, 1961) and molybdenum was titrated by spectrophotometric method employing thiocyanate (Parker, 1983).

RESULTS AND DISCUSSION

At first stage we studied the transfer with solutions containing uranium and molybdenum separately. Experiments were carried out under 2.5 mA cm⁻² current density with different flows, 0.06, 0.12 and 0.18 L h⁻¹, of inlet solution. Time dependence of molybdenum amount at the outlet solution is reported in Fig. 2.

It is noted that the flow augmentation, raises molybdenum concentration at the outlet. It can be explained by the fact that contact time of diluat solution in resin decreases when flow rate increases. For the three tests displayed in Fig. 2, circulation velocity in central compartment diluat varies from 0.0926 to 0.277 cm sec⁻¹. These experiments demonstrate that for identical operating conditions, molybdenum amount in the outlet increases three times more when flow rate fluctuates from 0.06 to 0.18 L h⁻¹. The amount of molybdenum is 35 and 90%, respectively.

The Fig. 3 shows the time dependence of uranium amount at 0.06 L h⁻¹. At the starting of the experiment, the uranium is mainly transferred by electric current into the receiver compartment. Then the fixation and the transfer take place. Above 45 min the amount of uranium in the outlet keeps a constant value.

The formation of chlorocomplexes of UO₂²⁺ are given by Eq. 1 however the Cl⁻ concentration of UO₂ Cl₂

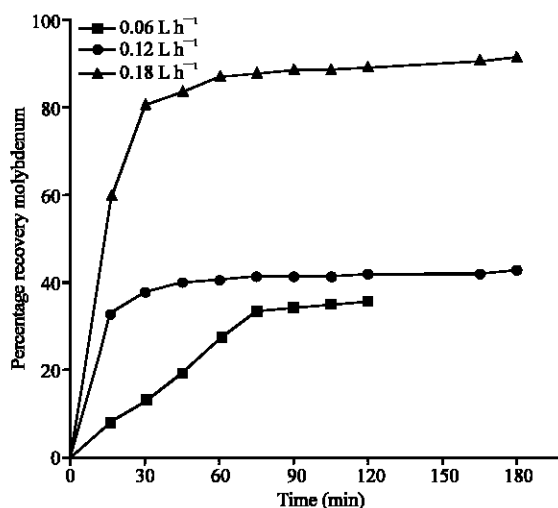


Fig. 2: Time dependence of the amount of molybdenum at the outlet compartment under 2.5 mA cm⁻² current density

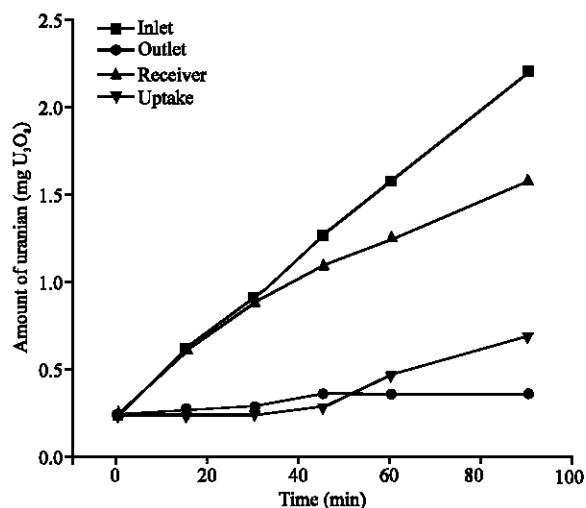
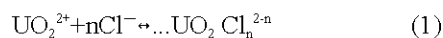
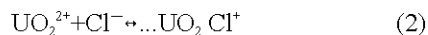


Fig. 3: Time dependence of uranium amount (U_3O_8) at the inlet and outlet and receiver compartment under 2.5 mA cm^{-2} current density

and $\text{UO}_2 \text{Cl}_2$ ions are insignificant in acidic chloride solution when the Cl^- concentration is lower than 1 M.



The first chlorocomplex gives:



The Fig. 4 shows the diagram of uranium species in hydrochloric acid medium. We observe that for pH values between 1 and 1.5 the UO_2^{2+} species predominate.

The Fig. 5 and 6 show the amount variation of uranium and molybdenum as for their percentage recovery. The molybdenum separation possibility from uranium solution by EDIR is demonstrated. The selectivity factor, r , was higher than 3, implying that the recovery of uranium is higher than the one of molybdenum. This factor, for molybdenum versus uranium is defined here as the ratio of the fluxes of the ionic species MoO_2^{2+} and UO_2^{2+} divided by the ratio of the mean concentration in the inlet solution.

$$r = \frac{J_{\text{MoO}_2^{2+}} \cdot C_{\text{inlet}}^{\text{UO}_2^{2+}}}{J_{\text{UO}_2^{2+}} \cdot C_{\text{inlet}}^{\text{MoO}_2^{2+}}}$$

Considering the obtaining of an equilibrium state of the system, we have carried out a long duration handling of 10 h. The Fig. 7 shows That on the one hand the slope 1 of the $N_{\text{in}}(\text{Mo})$ and $N_{\text{out}}(\text{Mo})$ straight lines are being equal, the kinetics of admission and transfer of the

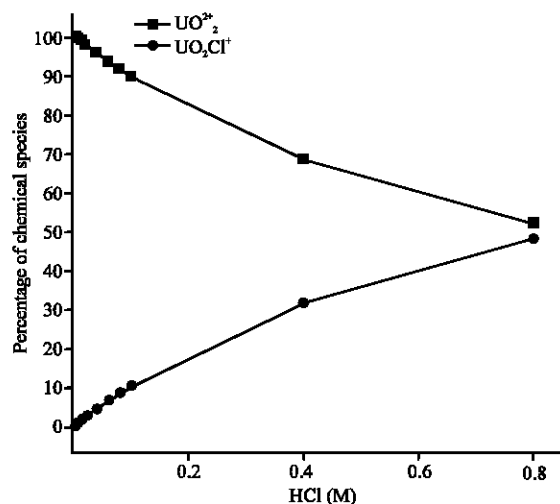


Fig. 4: Percentages of various chemical species in acidic uranyl chlorid solution

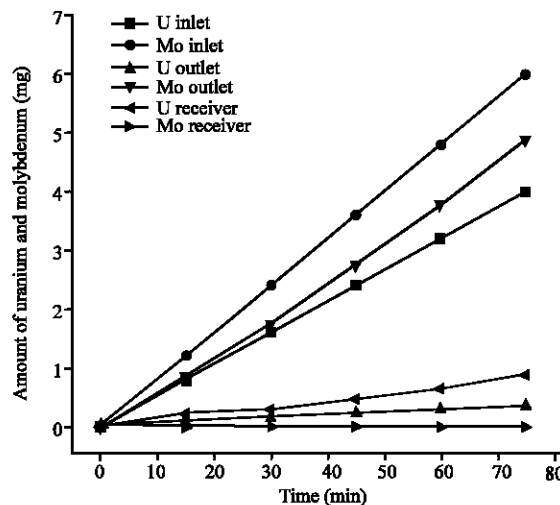


Fig. 5: Variation with time of the amount of uranium and molybdenum from the feed solution

MoO_2^{2+} ions are identical, after 10 h we obtain a removal efficiency for molybdenum higher than 98%. On the other hand the amount of N_{out} (uranium) keeps a constant value. At time t , $N_{\text{in}}(\text{Mo})$ is the amount of molybdenum in the inlet solution, $N_{\text{out}}(\text{Mo})$ is the amount of molybdenum in the outlet solution. At the beginning of the experiment the cell voltage is 6 V, then stabilizes to a constant value of 10 V (Fig. 8).

The chemistry of the molybdenum in solution is particularly complex. In neutral or lowly acidic environment the molybdenum is present as molybdates or paramolybdates. In acidic solution ($\text{pH} < 6$) we will have especially molybdic acid species. In dilute solution of

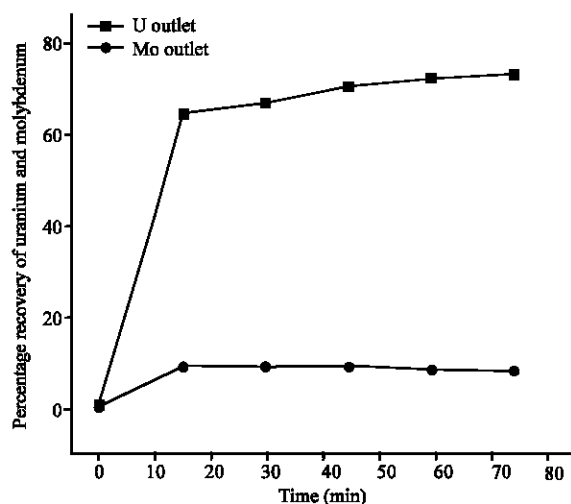


Fig. 6: Variation with time of recovery percentage of uranium and molybdenum

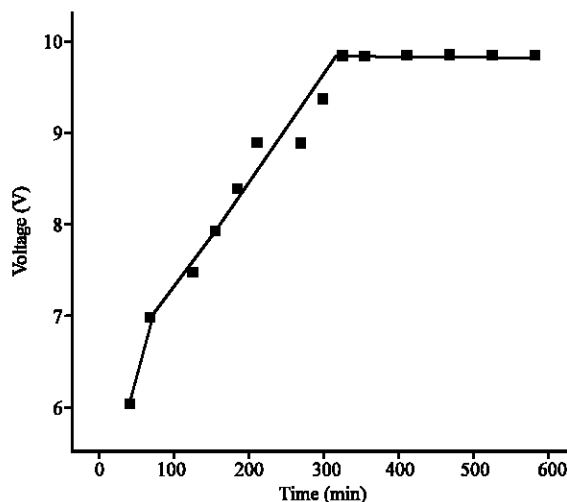


Fig. 8: Time dependence of the cell voltage during 600 min

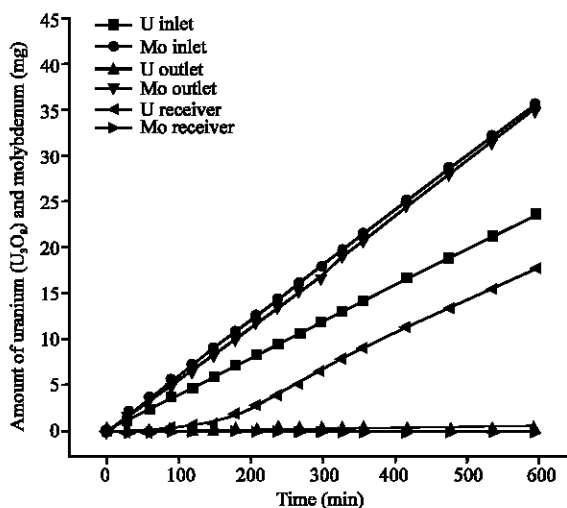


Fig. 7: Variation with time of amount of uranium and molybdenum from the feed solution (600 min)

molybdenum, there can exist tetramolybdic acid (Merrit, 1971). When we add progressively chlorhydric acid in molybdic acid solution, Mo^{VI} ion passes progressively to the state of molybdyl cations to which we assign a monomer form: MoO_2^{2+} and MoO_2OH^+ (Matsuda and Abiao, 1973). In identical conditions other authors conclude the existence of paramolybdate and possibly their protonated forms. In hydrochloric acidic solution (concentration >1 M), most authors agree on the fact that only MoO_2^{2+} and MoO_2Cl^+ represent a sufficient stability (Charlot, 1963). The results obtained by Lorang (Lorang and Kinh, 1970) show that chemical species of

molybdenum depend on the ratio $\text{M}_0^{\text{VI}}/\text{H}^+$. and there are some difficulties to determine it, because of the easiness for molybdenum to give polycation and polyanion species.

Let's note that the outlet concentration of the feed solution is lower than 1.5 mg L^{-1} (U_3O_8). It had been proved experimentally by many authors that the affinity of ions for the same resin increases with the ion charge in a diluted solution with a concentration below 0.1 M. Polyvalent ions are fixed better than monovalent ions. It should be that the affinity increases with: ion charge, ion size and atomic number. So the electroextraction efficiency depends on two parameters, the affinity of the regeneration cations for the sulfonate groups of resin and their mobility. Basically, for the cation exchangers with this functional groups, the selectivity sequence is $\text{H}^+ > \text{MoO}_2^{2+} > \text{UO}_2^{2+}$.

CONCLUSIONS

From the results of the present investigation, the major conclusions can be drawn. The electrically driven process combining ion-exchange resin and membranes, as developed in this study, could give improvements in the performances of both conventional ion exchange and electrodialysis. The possibility of separation of molybdenum from uranium solution by EDIR is demonstrated. The factor of selectivity, r , for molybdenum versus uranium is superior to 3. As important result we note that the concentration in radioactive element (U_3O_8) is lower than 1.5 mg L^{-1} . Small cell voltage is observed. The value doesn't pass 10 V.

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