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Electrotransport of Molybdenum Through an Electrodialysis Membrane. 
Concentration and Potential Profiles in Aqueous Interfacial Layers

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Abstract: In the first part we have observed the electrotransport of molybdenum in carbonate media 
(OH\(^-\), CO\(_3^{2-}\)) through a commercial electrodialysis anion exchange membrane. The values of the molybdenum, 
hydrogen oxide and carbonate fluxes obtained in this study show that molybdenum is present as molybdate 
ion MoO\(_4^{2-}\) in carbonate solution and that the molybdyl tricarbonate ion hypothesis MoO\(_3\)(CO\(_3\))\(^3-\) 
a n't no longer be maintained. In order to confirm this result we have studied the electrotransport of molybdenum 
and carbonate ions with different CO\(_3^{2-}/\)MoO\(_4^{2-}\) ratio. The used theory is based on the fact that, the concentration 
 ratio in the membrane equals the one of the same species within the solution. These hypothesis have to be 
justified given that this equality is actually usual for unstirred layers extremity. Therefore, in the second part 
the concentration and the potential profiles in aqueous interfacial layers were determined by a numerical 
resolution of the Nernst-Planck electrodiffusion equation coupled with the Poisson equation. The obtained 
concentration profiles from numerical resolution differ from 3 to 6% from the ones acquired by analytical 
resolution method assuming the constant electrical field hypothesis for OH\(^-\), CO\(_3^{2-}\) ions, respectively. However 
the potential profiles display that constant electrical field hypothesis is strictly valid.

Key words: Electrodialysis, ion-exchange membranes, ion-transfer

INTRODUCTION

The objective of this study was to investigate the 
electrotransport of molybdenum in the multi-ionic system 
NaOH/Na\(_2\)CO\(_3\)/Na\(_4\)MoO\(_4\). In the first part we have observed the electrotransport of molybdenum and 
carbonate ions through a commercial electrodialysis anion exchange membrane. We used different 
CO\(_3^{2-}/\)MoO\(_4^{2-}\) ratios. In the second part the concentration 
and the potential profiles in aqueous interfacial layers were determined by a numerical resolution of the 
Nernst-Planck electrodiffusion equation coupled with the Poisson equation.

At the time of the Nernst-Planck and Poisson 
equations resolution several important problems are 
encountered: Transport in the regions where is no-zero 
charge density, flux of co-ion equal to zero, transport of 
solvent and ion-ion interaction and their impact on 
various transport phenomena when we studied the 
transport in multi-ionic systems. For the participation 
of the natural convection, it seems that this phenomenon is 
less important with the anion exchange membrane. These 
membranes are known for rising water splitting process 
(Zabolotski et al., 1985); Transport problem treatment in 
multi-ionic system seems to be demanding regarding 
umerical techniques. Consequently several numerical 
methods for Nernst-Planck solution and Poisson equation 
system have been reported previously. As mentioned by 
certain authors (Choi and Moon, 2002) there is no 
umerical procedure applied to the description of ionic 
transport through both membrane and unstirred layers that takes into consideration the mentioned 
problems. The resolutions of boundary problems are done 
with considerable mathematical difficulties, especially 
if the transport involved more then two sorts of ions 
(Lebedev, 1999). Other problems arise from the 
mathematical complexity of the coupled differential 
equation ruling transport. Many researchers have solved 
the governing equations using simplifying assumptions 
such as electroneutrality (\(\rho = 0\)), constant field condition 
(Lim, 2007). His goal is to develop a Finite Element 
Method (FEM) to solve the NPF equations (Nernst-
Planck-Poisson).

In this present study we propose an interpretative 
model. This model is based on the one hand on 
electrodiffusion equations and on the other hand on the
fact that concentration amount ratio of both species in the membrane equals the one of the species it selves within the solution. This theory will be employed to elucidate the independence or the interdependence of CO₃⁻ ion and molybdenum. However this hypothesis have to be justified given that this equality is actually usual for unstirred layers extremity. That’s why, the concentration and the potential profiles in aqueous interfacial layers (multi-ionic system NaOH/Na₂CO₃/Na₂MoO₄) were determined by a numerical resolution of the Nernst-Planck electrodiffusion equation coupled with the Poisson equation for. We consider two cases, the constant and variable electrical fields. The non-conformity of the electric field in the unstirred layers incites to take into consideration the space charges in this layer, that can’t be neglected. The density of space charges is proportional to \( \sum C_i \). Concerning the flux of co-ion we have used the radiotracers to underline an eventual leak. Unidirectional ions flux values are calculated from sample radioactivity variation, measured by spectrometry \( \gamma \) (Packard Auto Gamma 500C). The acquired results display that the co-ion Na⁺ leak through the anions exchange membrane is a negligible phenomenon.

The numerical resolution used requires the following steps: discretization, linearization by the Newton method then the resolution by a direct method.

This theme of research which concerns the purification of the carbonate leach solutions of the uranium ores by electrodialysis process has been investigated since 1994 in the laboratory of analysis (Nuclear Research Center of Draria).

The first results have been presented during the international congress on membranes and membrane process (Lounis, 2002).

**MATERIALS AND METHODS**

Laboratory electrodialysis cells, as well as the experiment procedure and titration method of OH⁻, CO₃⁻ and HCO₃⁻, have been previously described (Lounis, 1997). The effective area of each membrane and each electrode is 10 cm². An ASTI pump provides the solution dilution flow; its initial volume is 100 mL. The current density is 20 mA cm⁻². The cell, schematically represented in Fig. 1, is composed of five compartments, that are separated by ion exchange membranes. In the central compartment \( P \), a solution containing OH⁻, CO₃⁻, and MoO₄⁻, anions was circulating.

The membranes used are Selemion AMV (anion exchange membrane) and CMV (cation exchange membrane) produced by Asahi Glass. Sampling is made in the central and anodic compartment at regular intervals of time. Molybdenum is titrated by spectrophotometric method using thiocyanate (Gordon and Parker, 1983).

**RESULTS AND DISCUSSION**

On Fig. 2 are represented the number variations of moq of OH⁻ and CO₃⁻ ions transferred from the diluate of which initial compositions are NaOH 0.125 eq L⁻¹ and Na₂CO₃ 0.13 eq L⁻¹ to the anodic concentrate. From the obtained straight lines, we can deduct that during the two hours the flux represent 88% of the total current that is carried by these two ions. The flux of electrical charges carried by OH⁻ ions is almost two times higher than the one carried by CO₃⁻ ions.

It results that in the central compartment, after two hours of ED, the concentration of OH⁻ ions is 10 times lower than that of CO₃⁻ while at initial time the concentration of these two ions was practically identical.

The Fig. 3 demonstrates that the transfer of hydroxyl ions (OH⁻) is not modified by the presence of molybdenum ions. However, the electrotransport of carbonate ions is altered. During 90 min of ED we have obtained similar result with the former case, the concentration of OH⁻ ions is 10 times smaller than that of CO₃⁻. The percentage of ions recovery are 72, 33 and 13% for OH⁻, MoO₄⁻, and CO₃⁻, respectively.

These results allow us to claim the following conclusion: The molybdenum is present in alkaline solution as the molybdate ion (MoO₄²⁻) form, in case of the existence of molybdyl ion MoO₂(CO₃)⁺, we should observe a higher transfer of CO₃⁻ ions. This result is similar to that of Pascal (1959). The action of an excess hard base on the molybdenum gives in the solution a molybdate ion when the ratio of MoH/MoO₂ >2, in our case this ratio is as high as 6.
In order to confirm this result we have studied the electrotransport of molybdenum and carbonate ions with different [CO$_3^{2-}$]/[MoO$_4^{2-}$] ratio. The ratios are 1.16, 3.5, 7.33, 10, 14.5 and 18.29. The Fig. 4-9 assert these results.

The following assumptions are made to analyze the obtained data:

- Electro neutrality holds in all part of the membrane-solution system.
- The two layers on both sides of the solution-membrane interface are in quasi equilibrium data.
- The diffusion term is neglected.

The Nernst-Planck electrodiffusion equation is

$$J_i = -D_i \left[ \frac{dC_i}{dx} + z_i \frac{F}{RT} \frac{d\Phi}{dx} \right]$$  \hspace{1cm} (1)
Fig. 7: Variation vs. time of the $\text{CO}_3^{2-}$ and $\text{MoO}_4^{2-}$ ions leaving the central compartment. $[\text{CO}_3^{2-}]/[\text{MoO}_4^{2-}] = 10$

Fig. 8: Variation vs. time of the $\text{CO}_3^{2-}$, $\text{OH}^-$ and $\text{MoO}_4^{2-}$ ions leaving the central compartment. $[\text{CO}_3^{2-}]/[\text{MoO}_4^{2-}] = 14.5$

Fig. 9: Variation vs. time of the $\text{CO}_3^{2-}$, $\text{OH}^-$ and $\text{MoO}_4^{2-}$ ions leaving the central compartment. $[\text{CO}_3^{2-}]/[\text{MoO}_4^{2-}] = 18.3$

$J_i$ = Flux of $i$ ion across the exchange membrane (g eq cm$^{-2}$ s$^{-1}$)
$D_i$ = Diffusion coefficient of ion (cm$^2$ s$^{-1}$)
$C_i$ = Concentration of $i$ ion (g eq L$^{-1}$)
$F$ = The Faraday constant (C)
$R$ = The gas constant (J mole K$^{-1}$)

$T$ = The absolute temperature (K)
$\Delta\phi/\Delta x$ = The gradient of electrical potential

Under this assumptions the Nernst-Planck electrodiffusion equation becomes:

$$J_i = u_i^m q_i C_i \frac{\Delta\phi}{\Delta x}$$  \hspace{1cm} (2)

The Nernst Einstein relation relates the mobility of the species $i$ to its diffusion coefficient:

$$D_i^m = \frac{RT}{F} q_i u_i^m$$  \hspace{1cm} (3)

Equation 1 and 2 give

$$J_i = -\frac{F}{RT} D_i^m q_i C_i \frac{\Delta\phi}{\Delta x}$$  \hspace{1cm} (4)

From the Eq. (3) the expressions of $J_{\text{MoO}_4^{2-}}$ and $J_{\text{CO}_3^{2-}}$ are:

$$J_{\text{MoO}_4^{2-}} = \frac{F}{RT} D_{\text{MoO}_4^{2-}} q_{\text{MoO}_4^{2-}} C_{\text{MoO}_4^{2-}} \frac{\Delta\phi}{\Delta x}$$  \hspace{1cm} (5)

$$J_{\text{CO}_3^{2-}} = \frac{F}{RT} D_{\text{CO}_3^{2-}} q_{\text{CO}_3^{2-}} C_{\text{CO}_3^{2-}} \frac{\Delta\phi}{\Delta x}$$  \hspace{1cm} (6)

The ratio of these fluxes gives

$$\frac{J_{\text{MoO}_4^{2-}}}{J_{\text{CO}_3^{2-}}} = \frac{D_{\text{MoO}_4^{2-}}^m q_{\text{MoO}_4^{2-}}}{D_{\text{CO}_3^{2-}}^m q_{\text{CO}_3^{2-}}}$$  \hspace{1cm} (7)

In which the concentration ratio inside the membrane can be replaced by the concentration ratio in the bulk.

$$\frac{C_{\text{MoO}_4^{2-}}}{C_{\text{CO}_3^{2-}}} = \frac{c_{\text{MoO}_4^{2-}}}{c_{\text{CO}_3^{2-}}}$$  \hspace{1cm} (8)

Thus

$$K = \frac{D_{\text{MoO}_4^{2-}}^m}{D_{\text{CO}_3^{2-}}^m} \frac{J_{\text{MoO}_4^{2-}}}{J_{\text{CO}_3^{2-}}}$$  \hspace{1cm} (9)

$$\frac{J_{\text{MoO}_4^{2-}}}{J_{\text{CO}_3^{2-}}} = K \frac{C_{\text{MoO}_4^{2-}}}{C_{\text{CO}_3^{2-}}}$$  \hspace{1cm} (10)

On the Fig. 10 the value of $J_{\text{MoO}_4^{2-}}/J_{\text{CO}_3^{2-}}$ were plotted as a function of $C_{\text{MoO}_4^{2-}}/C_{\text{CO}_3^{2-}}$. The values show that the
transport theoretical model used is satisfied at different concentration ratios. A proportional variation is obtained as might be expected from Eq. 10.

**Concentration and potential profiles:** Since necessary factors to resolve the Nernst-Planck equation within the membrane are being unknown, we will only study the ions electrotransport in the unstirred layers (Nernst-Planck film) close to the membrane.

The Nernst Planck equation is resolved keeping in mind, on one hand that the electrical field is constant and on the other hand using the Poisson equation, which explains the distribution of electrical charges. For the NaOH/Na2CO3/Na2MoO4 system, the Nernst-Planck electrodiffusion equation in general feature gives:

\[
J_{\text{OH}^-} = -D_{\text{OH}^-} \left[ \frac{dC_{\text{OH}^-}}{dx} - \frac{C_{\text{OH}^-} F \phi}{RT} \right]
\]

\[
J_{\text{CO}_3^-} = -D_{\text{CO}_3^-} \left[ \frac{dC_{\text{CO}_3^-}}{dx} - \frac{2C_{\text{CO}_3^-} F \phi}{RT} \right]
\]

\[
J_{\text{MoO}_4^{2-}} = -D_{\text{MoO}_4^{2-}} \left[ \frac{dC_{\text{MoO}_4^{2-}}}{dx} - \frac{2C_{\text{MoO}_4^{2-}} F \phi}{RT} \right]
\]

\[
J_{\text{Na}^+} = -D_{\text{Na}^+} \left[ \frac{dC_{\text{Na}^+}}{dx} + \frac{C_{\text{Na}^+} F \phi}{RT} \right]
\]

(It can be checked that \( J_{\text{Na}^+} = 0 \))

The relation between potential and distribution of electrical charges is ruled by the Poisson equation.

\[
\frac{d^2 \phi}{dx^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r}
\]

Where, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) the relative permittivity, \( \phi \) the electrical potential and \( \rho \) the local charge density defined as:

\[
\rho(x) = F \left( \sum_i C_i(x) - N(x) \right)
\]

\( N(x) \) is the concentration of fixed charges.

\[\rho = (C_{\text{Na}^+} - 2C_{\text{CO}_3^-} - 2C_{\text{MoO}_4^{2-}} - C_{\text{OH}^-})F \] in a medium with no fixed charge distribution.

Reduced variables are defined to resolve the different equations.

\[\zeta = \frac{x}{\delta}, \quad \frac{\delta \phi}{d \zeta} = \frac{F \phi}{RT}, \quad \sigma = \frac{\varepsilon_0 \varepsilon_r RT}{N_0 F^2 \delta^2}
\]

\[\text{OH} = \frac{C_{\text{OH}^-}(x)}{N_0}, \quad \text{CO} = 2 \frac{C_{\text{CO}_3^-}(x)}{N_0}, \quad \text{MO} = 2 \frac{C_{\text{MoO}_4^{2-}}(x)}{N_0}
\]

\[\text{NA} = \frac{C_{\text{Na}^+}(x)}{N_0}\]

Where, \( N_0 \) is the normality of the bulk solution expressed in mol cm\(^{-3}\).

The membrane solution interfaces are given in Fig. 11.

With the reduced variables the above system of equation becomes:

\[\text{OH} + \text{CO} + \text{MO} - \text{NA} + \sigma \frac{d^2 \phi}{d \zeta^2} = 0\]

\[\frac{d \text{OH}}{d \zeta} - \text{OH} \frac{d \phi}{d \zeta} + \alpha = 0\]

\[\frac{1}{2} \frac{d \text{CO}}{d \zeta} - \text{CO} \frac{d \phi}{d \zeta} + \beta = 0\]

\[\frac{1}{2} \frac{d \text{MO}}{d \zeta} - \text{MO} \frac{d \phi}{d \zeta} + \gamma = 0\]

\[\frac{d \text{NA}}{d \zeta} + \text{NA} \frac{d \phi}{d \zeta} = 0\]

Where the unknown factors are \( \text{OH}, \text{CO}, \text{MO}, \text{NA} \) and \( \phi \) and the boundary conditions are:

\( \text{OH}_0 = \text{OH}_2 = 0, \quad \text{CO}_0 = \text{CO}_2 = 0, \quad \text{MO}_0 = \text{MO}_2 = 0 \)

\( \text{NA}_0 = \text{NA}_2 = 0, \quad \phi_0 = 0, \quad \phi_2 = V \)
Fig. 11: Concentration profiles in unstirred layers (schematic)

\[ J_{\text{Na}^+} = J_{\text{OH}^-} = J_{\text{CO}_3^-} \]
and \( \delta \) being constant the same for \( \alpha, \beta \) and \( \gamma \).

With \( \alpha = \frac{J_{\text{OH}^-}}{N_D \cdot D_{\text{OH}^-}} \), \( \beta = \frac{J_{\text{CO}_3^-}}{N_D \cdot D_{\text{CO}_3^-}} \), \( \gamma = \frac{J_{\text{MoO}_4^-}}{N_D \cdot D_{\text{MoO}_4^-}} \)

**Case where the electrical field is constant:** The concentration profiles are obtained by resolving the system of equations differential in first order with constant coefficients, which solutions are:

\[ \text{OH} = (\text{OH}_0 - \frac{\alpha}{\theta}) \exp(\theta \xi) + \frac{\alpha}{\theta} \]  
\[ \text{CO} = (\text{CO}_0 - \frac{\beta}{\theta}) \exp(\theta \xi) + \frac{\beta}{\theta} \]  
\[ \text{MO} = (\text{MO}_0 - \frac{\gamma}{\theta}) \exp(\theta \xi) + \frac{\gamma}{\theta} \]  
\[ \text{NA} = \text{NA}_0 \exp(-\chi \xi) \]

With \( \chi = \frac{\delta}{\xi} \)

Replacing the expressions \( \text{OH}; \text{CO}; \text{MO} \) and \( \text{NA} \) in the electroneutrality Eq 17 we get a third degree equation in which the unknown \( \theta \) appears both in the exponential term and in the quotient.

\[ (\text{OH}_0 - \frac{\alpha}{\theta}) \exp(2\theta \xi) + (\text{CO}_0 + \text{MO}_0 - \frac{\beta}{\theta} - \frac{\gamma}{\theta}) \exp(3\theta \xi) + \frac{\alpha + \beta + \gamma}{\theta} \exp(\theta \xi) - \text{NA}_0 = 0 \]  

This equation presents a non-linearity. It is solved by the dichotomy method (Press et al., 1992) for a given value of \( \xi \). Then, we obtain the concentration profiles. The potential profiles are obtained from:

\[ \frac{d\Phi}{dx} = -\frac{RT}{F \Phi} \]  

The following parameters were used for the calculations:
\[ D_{\text{OH}} = 5.31 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}; \delta = 2.25 \times 10^{-3} \text{ cm} \]
\[ D_{\text{MoO}_4^-} = 0.995 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}; R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}; \]
\[ D_{\text{CO}_3^-} = 0.925 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}; T = 294 \text{ K} \]
\[ F = 9.6485 \text{ C mol}^{-1} \]

**Case where the electrical field is not constant:** The numerical resolution used requires the following steps:

- Discretization with the finite difference method
- Linearization by the Newton method
- Equation system is solved using a direct method

We note a slight discrepancy between the profiles obtained from the Nernst-Planck-Poisson equation solution and those obtained with the resolution of equation using the constant electrical field hypothesis.

The result accords with those proposed by Taky (1991) and Chapotot (1994) where the difference appears from a current density over or equal to 20 mA cm\(^{-2}\).

In the anodic interfacial layer the concentration and potential profiles are given in the Fig. 12-15 for the studied ratio \( \frac{[\text{CO}_3^-]}{[\text{MoO}_4^-]} = 14.5 \) and \( \frac{[\text{CO}_3^-]}{[\text{MoO}_4^-]} = 18.3 \), respectively with the AMV Sellemion membrane.

We observe that in the present conditions (current density 20 mA cm\(^{-2}\) and complete concentration equal 0.265 mol L\(^{-1}\)) the concentration profiles obtained from numerical resolution differ about 3 to 6% from the values obtained by the analytical resolution method assuming the constant electrical field hypothesis for \( \text{OH}, \text{CO}_3^- \) ions, respectively. However, the potential profiles show that the constant electrical field hypothesis is strictly valid.

The concentration of \( \text{OH}^- \) in the diffusion layer decreases near the interface.

The concentration diminution of \( \text{CO}_3^- \) and \( \text{MoO}_4^- \) ions near the membrane surface shows that those ions transfer across the membrane in spite of their
ions in the solution increases the CO$_3^{2-}$ ions it contributes more to current transport and the concentration of CO$_3^{2-}$ decreases in the interface layer. This result is also confirmed with the percentage recovery of CO$_3^{2-}$ ions which is 51 and 60.05%, respectively for both cases

\[
\frac{[\text{CO}_3^{2-}]}{[\text{MoO}_4^{2-}]} = 14.5 \text{ and } 18.3.
\]

**CONCLUSION**

- The elimination of carbonate and molybdenum ions from aqueous solution can be easily performed by electrodialysis.
- The electrotransfer of molybdenum ion shows that molybdate ion is present in alkaline solution.
- The high values of the molybdenum flux obtained in this study show that electrodialysis can be used as a separation technique for molybdenum extraction.
- The results reported here indicate that the best value of the ratio CO$_3^{2-}$ for molybdenum extraction through an anion exchange membrane is 1.16.
- The concentration profiles obtained from numerical resolution differ in 3 and 6% from to the values obtained by the analytical resolution method assuming the constant electrical field hypothesis for OH$^-$, CO$_3^{2-}$, respectively. Meanwhile the potential profiles show that the constant electrical field hypothesis is strictly valid.
REFERENCES


