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MATHEMATICAL MODELING FOR THE EXTRACTION OF URANIUM AND MOLYBDENUM WITH EMULSION LIQUID MEMBRANE, INCLUDING INDUSTRIAL APPLICATION AND COST EVALUATION OF THE URANIUM RECOVERY

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ABSTRACT

Emulsion liquid membrane systems are double emulsion drops. Two immiscible phases are separated by a third phase which is immiscible with the other two phases. The liquid membrane systems were classified into two types: (1) carrier mediated mass transfer, (2) mass transfer without any reaction involved. Uranium extraction, molybdenum extraction and solvent extraction were used as purposed elements for each type of the membrane systems in the derivation of their mathematical models.

Mass transfer in emulsion liquid membrane (ELM) systems has been modeled by several differential and algebraic equations. The models take into account the following : mass transfer of the solute from the bulk external phase to the external phase-membrane interface; an equilibrium reaction between the solute and the carrier to form the solute-carrier complex at the interface; mass transfer by diffusion of the solute-carrier complex in the membrane phase to the membrane-internal phase interface; another equilibrium reaction of the solute-carrier complex to release the solute at the membrane-internal phase interface into the internal phase.

Models with or without the consideration of film resistances were developed and compared. The models developed in this study can predict the extraction rate through emulsion liquid membranes theoretically. All parameters required in the models can be determined before an experimental extraction run. Experimental data from literature (uranium extraction) and (molybdenum extraction and solvent extraction) were used to test the models. The agreements between the theoretical predictions and the experimental data were very good. The advantages of emulsion liquid membrane systems over traditional methods were discussed. The models developed in this research can be used directly for the design of emulsion liquid membrane systems. The results of this study represent a very significant step toward the practical applications of the emulsion liquid membrane technology.

Keywords*: emulsion liquid membrane, uranium, molybdenum, mathematical modeling, D_2EHPA, mass transfer, span 80, batch process, recovery, cost*

INTISARI

Sistem membrane cair emulsi adalah tetesan-tetesan emulsi ganda. Dua fase tidak salng larut dipisahkan oleh sebuah fase ketiga yang tidak saling larut dengan kedua fase yang lainnya. Sistem membrane cair tersebut diklasifikasi menjadi dua tipe yaitu (1) transfer massa yang dimediasi pembawa, (2) transfer masa tanpa melibatkan reaksi. Ekstraksi Uranium, ekstraksi molybdenum, dan ekstraksi solven digunakan sebagai elemen-elemen yang dituju untuk setiap tipe system membrane didalam derivasi model-model matematikanya.

Transfer masa dalam system membrane cair emulsi (ELM) telah dimodelkan dengan beberapa persamaan differensial dan aljabar. Model-model ini mempertimbangkan hal berikut: transfer masa solute dari fase eksternal bulk ke interface membrane. Fase eksternal adalah reaksi kesetimbangan antara solute pada interface; transfer masa melalui difusi dari kompleks pembawa solute di fase membrane ke face interface internal membrane; reaksi kesetimbangan yang lain dari kompleks pembawa salute untuk membebaskan solute pada interface fase internal membrane ke dalam fase internal.

Model dengan/tanpa pertimbangan resistensi film dikembangkan dan disbandingkan. Model yang dikembangkan di dalam studi ini dapat memprediksi kecepatan ekstraksi melalui membrane cair emulsi secara teoritis. Semua parameter yang diperlukan dalam model dapat ditentukan sebelum ekstraksi eksperimental dijalankan. Data eksperimental dari literature (ekstraksi uranium) dan (ekstraksi molybdenum dan ekstraksi sol-

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ver) digunakan untuk menguji modelnya. Persesuaian prediksi teoritis dan data eksperimental adalah sangat bagus. Kelebihan sistem membrane cair emulsi dibandingkan metode tradisional telah didiskusikan. Model yang dikembangkan dalam riset ini dapat digunakan secara langsung untuk desain system membrane cair emulsi. Hasil studi ini menghadirkan langkah masju yang sangat signifikan ke aplikasi praktis atas teknologi membrane cair emulsi.

Kata kunci: membrane cair emulsi, uranium, molybdenum, model matematika, *D_2EHPA,*, transfer massa, *, span 80, batch process, recovery, biaya*

INTRODUCTION

The field of liquid membrane technology is currently undergoing a rapid expansion of the areas of both research and industrial separation techniques. Emulsion liquid membranes can be manipulated to selectively separate a specific solute from a mixture, and even to extract a solute against its concentration gradient. Emulsion liquid membrane systems are comprised of three liquid phases. Two of these are miscible with each other but separated by a third phase (the membrane phase) which is immiscible with both. Mass is transferred from one of the miscible phase across the liquid membrane to the second miscible phase. In general, liquid membranes are either supported or unsupported. Supported liquid membranes can be held in a porous structure or bounded on either side by two thin polymeric films. Emulsion (unsupported) liquid membranes are usually in the form of double emulsion drops. For a water/oil/water (W/O/W) system, it is the immiscible oil phase, separating the two aqueous phases. For an O/W/O system, the liquid membrane is the immiscible water phase which separates the two oil phases. The effectiveness of the emulsion liquid membrane process can be enhanced by utilizing a facilited transport mechanism to maximize both the flux through the membrane phase, and the capacity of the receiving phase for the diffusing species.

The aim of this paper is to study mass transfer modeling of uranium and molybdenum extraction though emulsion liquid membrane systems (ELM), where several differential and algebraic equations were derived considering the conditions of operation for the extraction of both uranium and molybdenum, for which the data were adapted from several literatures.

The emulsion liquid membrane process is unique and different from other membrane processes such as reverse osmosis or ultrafiltration. The membrane is a liquid phase involving an emulsion configuration. Emulsion liquid membranes (ELMs), also called surfactant liquid membranes are essentially double emulsions, i.e., water/oil/water (W/O/ W) systems or oil/water/oil (O/W/O) systems. For the W/O/W systems, the oil phase separating the two aqueous phases is the liquid membrane. For the O/W/O systems, the liquid membrane is the water phase that is between the two oil phases. Since their discovery over two decades ago, emulsion liquid membranes have demonstrated considerable potential as effective tools for a wide variety of separations. Two commercial applications are: the removal of zinc from wastewater in the viscose fiber industry and the removal of phenol from wastewater. Another application has been as a well control fluid for preventing well blowout and sealing loss zones in oil and gas wells. In addition to other proposed oil-field applications, ELMs also have potential utility as membrane reactors incorporating simultaneous separation and reaction processes. This utility includes the use of ELMs for controlling chemical reactions. The effectiveness of ELMs is a result of two facilitated mechanisms: type 1, in which the reaction in the receiving phase (the internal phase if the external phase is a feed) maintains a solute concentration of effectively zero; and type 2 (carrier facilitated transport), where the diffusing species is carried across the membrane phase by incorporating a 'carrier' compound (complexing agent or extractant) in the membrane phase. For both types of facilitated mechanisms, simultaneous extraction and stripping take place in a single step rather than two steps as in solvent extraction. As shown in following Figure (1), here two immiscible phases, water and oil for example, are mixed vigorously and emulsion droplets are formed (droplet size about 0.5-10 μm), which are stabilized by the addition of a surfactant.

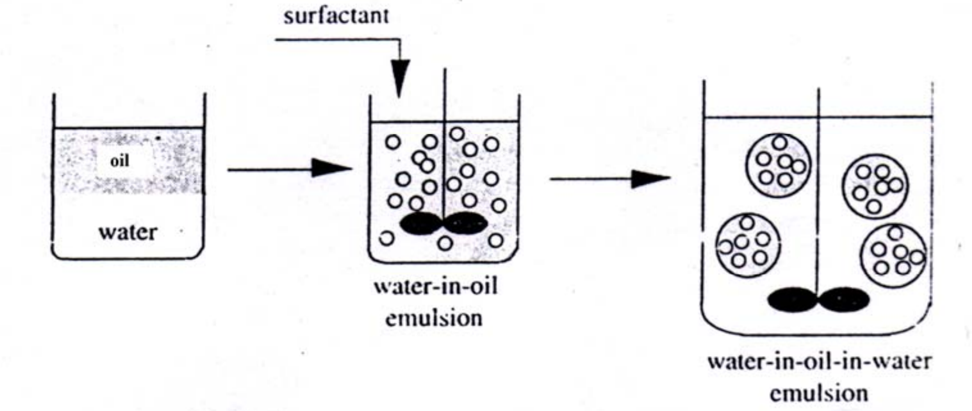

Fig. 1. Preparation of Emulsion Type Liquid Membrane (ELM)

In this research D$_2$EHPA (di-2-ethylhexyl phosphoric acid) is used as carrier to mediate the uranium and molybdenum extraction. The membrane phase consists of 2%W D$_2$EHPA (abbreviated as $(RH)_2$), 5%V surfactant Span 80 and the rest is kerosene. D$_2$EHPA is a water insoluble liquid ion exchange material, one which forms a strong and selective complex with uranium and molybdenum. The uranium and molybdenum ions are insoluble in the membrane phase but the complexes are soluble in the membrane phase. These complexes diffuse through the membrane and react with the strong acid in the internal receiving phase. The uranium and molybdenum ions are trapped and concentrated in the receiving phase. These concentrated uranium and molybdenum ion solution are then easier for recovery or disposal. After the reaction of the complexes and the strong acid, the carriers are reformed and diffuse back to the membrane external interphase. By properly controlling the pH values on both sides of the membrane, uranium can be extracted from the low concentration external phase to the high concentration internal phase.

Models with or without the consideration of film resistances were developed and compared. The models developed in this study can predict the extraction rate through emulsion liquid membranes theoretically. All parameters required in the models can be determined before an experimental extraction run. Experimental data from literature (uranium extraction) and (molybdenum extraction and solvent extraction) were used to test the models.

An overall extraction equilibrium formulations for uranium / molybdenum and D$_2$EHPA are expressed as follows:

$$\mathrm{UO_2^{2+} + 2(RH)_2 \longleftrightarrow [UO_2R_2\,2HR] + 2H^+}$$

$$\mathrm{MoO_2^{2+} + 2(RH)_2 \longleftrightarrow [MoO_2R_2\,2HR] + 2H^+}$$

Equilibrium constants can be expressed as follows:

$$\mathrm{K_{eq}} = \frac{[\overline{\mathrm{MoO_2R_2}\,2HR}][\mathrm{H}^+]^2}{[\mathrm{MoO_2^{2+}}][\overline{(\mathrm{RH})_2}]^2} \ldots(1)$$

$$\mathrm{K_{eq}} = \frac{[\overline{\mathrm{UO_2R_2}\,2HR}][\mathrm{H}^+]^2}{[\mathrm{UO_2^{2+}}][\overline{(\mathrm{RH})_2}]^2} \ldots(2)$$

Both the Membrane External and Internal Film Mass Transfer Resistances are Neglected. In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are neglected. From the principal of material balance the governing equations that describe the concentrations of

uranium, carrier and complex in each phases are (Bird et al., 1960):
Membrane phase:

$$(1\text{-}\varepsilon)\frac{\partial C_X}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{C_X}{r}\right)\right) - R_X \quad \ldots(3)$$

t =0 $C_X = 0$ for all r
r = 0 C_X = finite
r = R $C_X = C_X^*$

$$(1\text{-}\varepsilon)\frac{\partial C_{(RH)_2}}{\partial t} = D_{e(RH)_2}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{(RH)_2}}{\partial r}\right)\right) - 2R_X \quad \ldots(4)$$

t = 0 $C_{(RH)2} = C_{(RH)2O}$ for all r
r = 0 $C_{(RH)2}$ = finite
r = R $C_{(RH)2} = C_{(RH)2}^*$

External source phase:

$$V_t(1-\varphi')\frac{dCu}{dt} = N(4\pi R^2)D_{ex}\left(\frac{\partial C_X}{\partial r}\right)_{r=R} \quad \ldots(5)$$

t = 0 Cu=Cuo

Internal receiving phase:

$$\varepsilon\frac{\partial Cui}{\partial t} = R_X \quad \ldots(6)$$

t = 0 Cui = 0

After solving the above equations; considering the boundary conditions, the following mathematical models were obtained:

$$\frac{Cu}{Cuo} = \frac{3}{3 + m\Phi b} + \sum_{n=1}^{\infty}\frac{\tan(\beta_n)}{(1 + \frac{m\phi b}{2})\tan(\beta_n) + \frac{1}{2}\beta_n}e^{-\frac{\beta_n{}^2}{b}\tau} \quad \ldots(7)$$

$$b = 1 - \varepsilon + q\varepsilon \quad \ldots(8)$$

$$\tau = \frac{D_{ex}}{R^2}t \quad \ldots(9)$$

$$\phi = \frac{3\phi'}{1 - \phi'} \quad \ldots(10)$$

$$m = \frac{K_{eq}.C_{(RH)_2O}{}^2}{C_{HO}{}^2} \quad \ldots(11)$$

$$q = \frac{C_{HOi}{}^2}{K_{eq}.C_{(RH)_2O}{}^2} \quad \ldots(12)$$

β_n are eigen values of

$$\tan(\beta) = \frac{m\phi b\beta}{m\phi b + \beta^2} \quad \ldots(13)$$

Only the Membrane External Film Mass Transfer Resistance is Considered. In this case, the membrane external interphase mass transfer resistance is considered while the membrane internal interphase mass transfer resistance is neglected. The governing equations for the uranium extraction process are:
Membrane phase:

$$(1-\varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_x}{\partial r}\right)\right) - R_x \quad \ldots(14)$$

t=0 C_X=0 for all r
r=0 C_X=finite
r=R $C_X=C_X^*$

External source phase:

$$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu - Cu^*) \quad \ldots(15)$$

t=0 Cu=Cuo

After solving the above equations; considering the boundary conditions, the following mathematical models were obtained:

$$\frac{cu}{Cuo} = \frac{3}{3 + m\phi b} + \sum_{n=1}^{\infty}\frac{(1 - mK_o)\tan(\beta_n) + mK_o\beta_n}{(1 - mK_o - \frac{1}{2}mK_o\beta_n{}^2 + \frac{1}{2}m\phi b)\tan(\beta_n) + (\frac{1}{2} + mK_o)\beta_n}e^{-\frac{\beta_n{}^2}{b}\tau} \quad \ldots(16)$$

$$b = 1\text{-}\varepsilon\text{+}q\varepsilon \quad \ldots(17)$$

$$\tau = \frac{D_{ex}}{R^2}t \quad \ldots(18)$$

$$\phi = \frac{3\phi'}{1 - \phi'} \quad \ldots(19)$$

$$m = \frac{K_{eq}.C_{(RH)_2O}^{\;2}}{C_{HO}^{\;2}} \quad \text{...(20)}$$

$$q = \frac{C_{HOi}^{\;2}}{K_{eq}.C_{(RH)_2O}^{\;2}} \quad \text{...(21)}$$

$$K_O = \frac{D_{ex}}{Rk_o} \quad \text{...(22)}$$

β_n are eigen values of

$$\tan(\beta) = \frac{(m\phi b - mK_o\beta^2)\beta}{(1 - mK_o)\beta^2 + m\phi b} \text{ ...(23)}$$

Both the Membrane External and Internal Film Mass Transfer Resistance are Considered. In this case both the membrane external interphase mass transfer resistance and the membrane internal interphase mass transfer resistance are considered.

The governing eqns. for the uranium extraction process are:

Membrane phase: $(1 - \varepsilon)\frac{\partial C_x}{\partial t} = D_{ex}(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial C_x}{\partial r})) - k_i a(C_x - C_{xi}^*)$ ...(24)

t=0 C_X=0 for all r
r=0 C_X=finite
r=R $C_X=C_X^*$

$$(1-\varepsilon)\frac{\partial C_{(RH)_2}}{\partial t} = D_{e(RH)_2}(\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial C_{(RH)_2}}{\partial r})) - 2k_i a(C_x - C_{xi}^*) \quad \text{...(25)}$$

t=0 $C_{(RH)2} = C_{(RH)2O}$ for all r
r=0 $C_{(RH)2}$ = finite
r=R $C_{(RH)2} = C^*_{(RH)2}$

External source phase:

$-V_t(1-\phi')\frac{dCu}{dt} = N(4\pi R^2)k_o(Cu - Cu^*)$ ...(26) t=0 Cu=Cuo

$N(4\pi R^2)k_O\ (Cu\text{-}Cu^*) = N(4\pi R^2)D_{ex}(\frac{\partial C_x}{\partial r})r=R$ ...(27)

After solving the above equations; considering the boundary conditions, the following mathematical models were obtained:

$$\frac{Cu}{Cuo} = \frac{3}{3 + m\phi b}$$

$$+ \sum_{n=1}^{\infty} \frac{[(1 - mK_o)\tan(h_n) + mK_o h_n]e^{-\beta_n\tau}}{[1 - mK_o + \frac{1}{2}(m\phi - \beta_n mK_o)(\frac{h_n^2}{\beta_n} - Q(-\beta_n))]\tan(h_n) + (\frac{1}{2} - \frac{\beta_n}{2h_n^2}Q(-\beta_n) + mK_o)h_n}$$

$$+ \sum_{j=1}^{\infty} \frac{[(1 - mK_o)\tan(h_j) + mK_o h_j]e^{-\gamma_n\tau}}{[1 - mK_o + \frac{1}{2}(m\phi - \gamma_j mK_o)(\frac{h_j^2}{\gamma_j} - Q(-\gamma_j))]\tan(h_j) + (\frac{1}{2} - \frac{\gamma_j}{2h_j^2}Q(-\gamma_j) + mK_o)h_j}$$

...(28)

$b = 1-\varepsilon+q\varepsilon$ ...(29)

$\tau = \frac{D_{ex}}{R^2}t$ ...(30)

$y = \frac{r}{R}$ ...(31)

$\phi = \frac{3\phi'}{1 - \phi'}$ ...(32)

$K_O = \frac{D_{ex}}{Rk_o}$ ...(33)

$K_i = \frac{D_{ex}}{R^2k_i a}$ ...(34)

$a = \frac{3\varepsilon}{d_r}$ ...(35)

$$m = \frac{K_{eq}.C_{(RH)_2O}{}^{2}}{C_{HO^2}} \quad \ldots(36)$$

$$q = \frac{C_{HOi}{}^{2}}{K_{eq}.C_{(RH)_2O}{}^{2}} \quad \ldots(37)$$

$$Q(s)=\frac{q^2\varepsilon^2 K_i s}{(q\varepsilon K_i s + 1)^2} \quad \ldots(38)$$

$$\tan(h) = \frac{(-\beta m K_o + m\phi)h}{m\phi + (1 - mK_o)\beta} \quad \ldots(39)$$

$$\tan(h) = \frac{(-\gamma m K_o + m\phi)h}{m\phi + (1 - mK_o)\gamma} \quad \ldots(40)$$

$$s^{+} = -\beta = \frac{-(b + q\varepsilon K_i h^2) + \sqrt{(b + q\varepsilon K_i h^2)^2 - 4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\varepsilon K_i} \quad \ldots(41)$$

$$s^{-} = -\gamma = \frac{-(b + q\varepsilon K_i h^2) + \sqrt{(b + q\varepsilon K_i h^2)^2 - 4(1-\varepsilon)q\varepsilon K_i h^2}}{2(1-\varepsilon)q\varepsilon K_i} \quad \ldots(42)$$

Solvent Extraction by Liquid Membrane Systems, Uranium and Molybdenum. In this process, liquid membrane is usually in O/W/O form and it can be used for solvent extraction of both uranium and molybdenum. Several assumptions were made to model the complicated batch process of solvent extraction by emulsion liquid membranes.

The governing equations for elements A (uranium) and B (molybdenum), and extract solvent C in each phase are as follows:

Membrane phase:

$$(1-\varepsilon)\frac{\partial C_A}{\partial t} = D_{eA}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)\right) + R_A \quad \ldots(43)$$

$t=t_O$ $C_A=C_{AO}$
$r=0$ $C_A=\text{finite}$
$r=R$ $C_A=C_A^{*}$

$$(1-\varepsilon)\frac{\partial C_B}{\partial t} = D_{eB}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_B}{\partial r}\right)\right) + R_B \quad \ldots(44)$$

$t=t_O$ $C_B=C_{BO}$
$r=0$ $C_B=\text{finite}$
$r=1$ $C_B=C_B^{*}$

$$(1-\varepsilon)\frac{\partial C_C}{\partial t} = D_{eC}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_C}{\partial r}\right)\right) + R_C \quad \ldots(45)$$

$t=t_O$ $C_C=C_{CO}$
$r=0$ $C_C=\text{finite}$
$r=R$ $C_C=C_C^{*}$

External extract phase:

$$\frac{dA}{dt} = -N(4\pi R^2)D_{eA}\left(\frac{\partial C_A}{\partial r}\right)_{r=R} \quad \ldots(46)$$

$t=t_O$ $A=A_O$

$$\frac{dB}{dt} = -N(4\pi R^2)D_{eB}\left(\frac{\partial C_B}{\partial r}\right)_{r=R} \quad \ldots(47)$$

$t=t_O$ $B=B_O$

$$\frac{dC}{dt} = -N(4\pi R^2)D_{eC}\left(\frac{\partial C_C}{\partial r}\right)_{r=R} \quad \ldots(48)$$

$t=t_O$ $C=C_O$

$$N = \frac{V_{E0}}{(4/3)\pi R_0^3} \quad \ldots(49)$$

Internal raffinate phase:

$$\varepsilon M_R \frac{X_A}{t} = -R_A \quad \ldots(50)$$

$t=t_O$ $X_A=X_{AO}$

$$\varepsilon M_R \frac{X_B}{t} = -R_B \quad \ldots(51)$$

$t=t_O$ $X_B=X_{BO}$

$$\varepsilon M_R \frac{X_C}{t} = -R_C \quad \ldots(52)$$

$t=t_O$ $X_C=X_{CO}$

Having the above parameter values, we can calculate A, B and C at next short time $t=t_1$. When we have the moles of A, B and C at time t_1, we can adjust the parameter values as follows:

$$C_{AO} = m_A M_m X_A = m_A M_m \frac{A_{Oi} - A}{A_{Oi} + B_{Oi} - A - B + C} \quad \ldots(53)$$

$$C_{BO} = m_B M_m X_B = m_B M_m \frac{B_{Oi} - B}{A_{Oi} + B_{Oi} - A - B + C} \quad \ldots(54)$$

$$C_{CO} = m_C M_m X_C = m_C M_m \frac{C}{A_{Oi} + B_{Oi} - A - B + C} \quad \ldots(55)$$

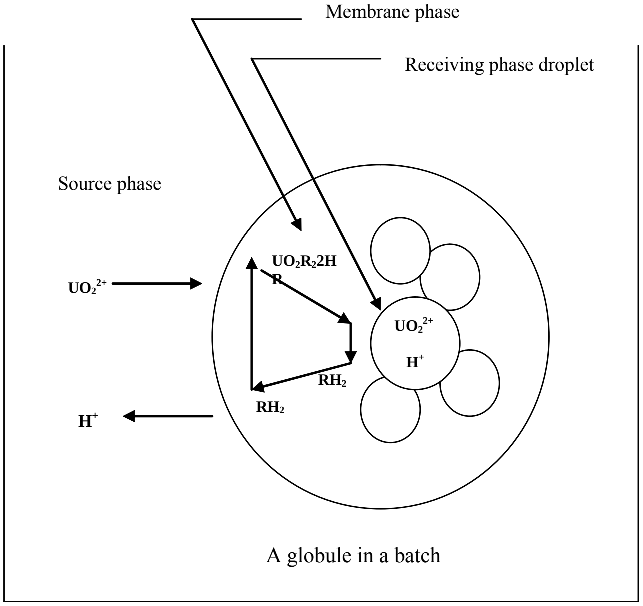

Fig. 2. Mechanism of Carrier Mediated Uranium Extraction through Emulsion Liquid Membranes

DISCUSSION

For both uranium and molybdenum extraction modeling process, several mathematical models have been developed in this research. For different cases of modeling, such as (1) when the internal film resistance is negligible:

$$\frac{Cu}{Cuo} = \lim_{K_i \to 0} \left[\frac{3}{3 + m\phi b} + \sum_{n=1}^{\infty} \frac{[(i - mK_o)\tan(h_n) + mK_o h_n]e^{-\beta_n \tau}}{[1 - mK_o + \frac{1}{2}(m\varphi - \beta_n mK_o)(\frac{h_n}{\beta_n} - Q(-\beta_n))]\tan(h_n) + (\frac{1}{2} - \frac{n}{2h_n^2}Q(-\beta_n) + mK_o)h_n} \right]$$

$$+\sum_{n=1}^{\infty}\frac{(1-mK_o)\tan(h_j)+mK_oh_je^{-\gamma_j}}{1-mK_o+\frac{1}{2}(m\phi-\gamma_jmK_o)(\frac{h_j}{\gamma_j}-Q(-\gamma_j))\tan(h_j)+(\frac{1}{2}-\frac{\gamma_j}{2h_j^2}Q(-\gamma_j)+mK_oh_j}\Bigg]$$

$$\frac{3}{3+m\phi b}+\sum_{n=1}^{\infty}\frac{(1-mK_o)\tan(h_n)+mK_oh_n}{(1-mK_o-\frac{1}{2}mK_oh_n^2+\frac{1}{2}mb)\tan(h_n)+(\frac{1}{2}+mK_o)h_n}e^{-\frac{h_n^2}{b}}$$

…(56)

(2) when the external film resistance is negligible:

$$\frac{Cu}{Cuo}=\lim_{K_o\to 0}\left[\frac{3}{3+m\phi b}+\sum_{n=1}^{\infty}\frac{(1-mK_o)\tan(\beta_n)+mK_o\beta_n}{(1-mK_o-\frac{1}{2}mK_o\beta_n^2+\frac{m\phi b}{2})\tan(\beta_n)+(\frac{1}{2}+mK_o)\beta_n}e^{-\frac{\beta_n^2}{b}}\right]$$

$$\frac{3}{3+m\phi b}+\sum_{n=1}^{\infty}\frac{\tan(\beta_n)}{(1+\frac{1}{2}m\phi b)\tan(\beta_n)+\frac{1}{2}\beta_n}e^{-\frac{\beta_n^2}{b}} \qquad \text{…(57)}$$

(3) solvent extraction:

$$C_{AO}=m_AM_mX_A=m_AM_m\frac{A_{Oi}-A}{A_{Oi}+B_{Oi}-A-B+C} \qquad \text{…(58)}$$

$$C_{BO}=m_BM_mX_B=m_BM_m\frac{B_{Oi}-B}{A_{Oi}+B_{Oi}-A-B+C} \qquad \text{…(59)}$$

$$C_{CO}=m_CM_mX_C=m_CM_m\frac{C}{A_{Oi}+B_{Oi}-A-B+C} \qquad \text{…(60)}$$

The mean diameter of globules and equilibrium constant were measured before uranium extraction. Diffusivities and mass transfer coefficients were estimated. The experimental conditions and all parameter values are summarized in Table 1 and Table 2. Having all the parameter values, with the aid of computer software (Mathematica 5.0), the above models will then be used to calculate the external phase uranium concentrations for different cases, and the results are shown in Figures 3 and 4.

Table.1 Experimental Conditions for Uranium Extraction

	Run 1	Run 2
Vol. of membrane phase, ml	40	40
Vol. of receiving phase, ml	40	40
Vol. of source phase, ml	460	460
Con. of UO_2 in source phase, ppm	130	174
Con. of HNO_3 in Rec. phase, %w	1.1	1.1
Mixing speed, rpm	280	280
pH value in Rec. phase	0.77	0.77
pH value in source phase	0.23	0.23

Table.2 Summarized Parameters Values for Uranium Extraction

	Run 1	Run 2
ε	0.5	0.5
ϕ'	0.148	0.148
ϕ	0.522	0.522
q	2169	2169
m	0.402	0.402
D_x, cm^2/sec	$7x10^{-7}$	$7x10^{-7}$
D_{UO2} (in kerosene)	$3.5x10^{-6}$	$3.5x10^{-6}$
R, cm	0.045	0.045
d_r, cm	0.0004	0.0004
k_o, cm/sec	0.0017	0.0017
k_i, cm/sec	0.0035	0.0035

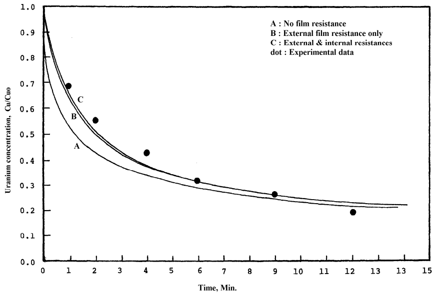

Fig. 3. Uranium Extraction – Run 1

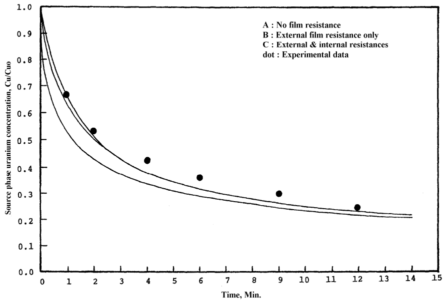

Fig. 4. Uranium Extraction – Run 2

Figure 5 shows the predictions and data for the mass fractions of A (uranium) and B (molybdenum) as a function of time. It can be seen from the Figure, when parameters were adjusted for every 0.125 hour, the predicted mass fraction of uranium in the extract phase is very close to the experimental date while the predicted mass fraction of molybdenum shows some deviation from data. For the curves indicated by $\Delta t=0.25$ shows some different results.

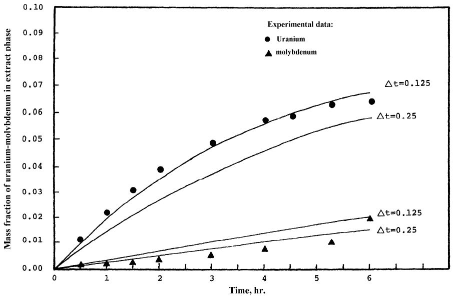

Fig. 5. Solvent Extraction

From the data, it seems that most of the leakage came at the time when the emulsion phase was breaking into small globules. After that initial period the leakage seems very slow. In practical applications, the 1% leakage rate is tolerable and is negligible

Effect of Carrier Concentration has shown from Figure 6, it can be said that at low carrier concentration, the increase of carrier concentration will increase the extraction rate. After certain optimum concentration, the increase of carrier concentration will have less effect on the uranium extraction rate.

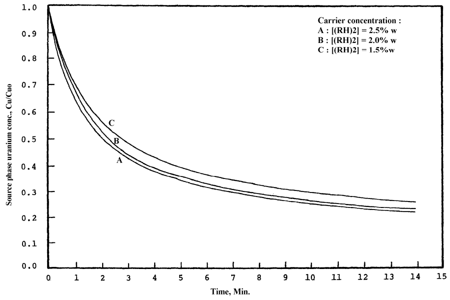

Fig. 6. Effect of Carrier Concentration on Uranium Extraction Rate

Figure 7 shows the effect of receiving phase nitric acid concentration on uranium extraction rate. If the nitric acid concentration is high, then the driving force between the membrane and the receiving phase will also be high, and so the extraction rate will be increased. But since the membrane rupture problem exists, the nitric acid concentration cannot be too high. Too much acid in the external aqueous solution will reduce the effectiveness of the liquid membrane systems.

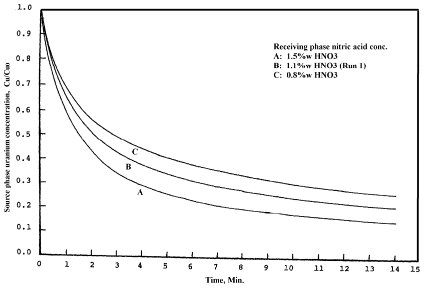

Fig. 7. Effect of Receiving Phase Concentration on Uranium Extraction Rate

Figure 8 shows the effect of Span 80 concentration on the molybdenum extraction rate. As shown in the Figure, higher surfactant concentration results in higher molybdenum extraction rate. But too much surfactant is not desirable, since it will cause some difficulty in breaking emulsion phase in a subsequent process.

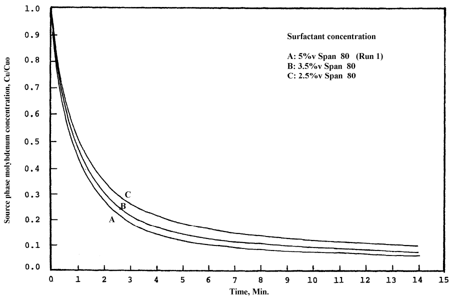

Fig. 8. Effect of Surfactant Concentration on Molybdenum Extraction Rate

The effect of NaOH concentration on the molybdenum extraction rate is similar to the nitric acid conc. on the uranium extraction rate. But again, because the leakage problem, the receiving phase NaOH concentration cannot be too high. Figure 9 shows the effect of NaOH concentration on the molybdenum extraction rate.

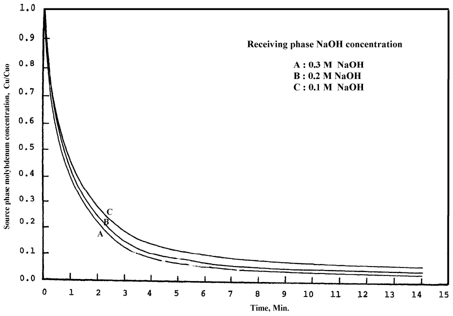

Fig. 9. Effect of Receiving Phase NaOH Concentration on Molybdenum Extraction Rate

Emulsion liquid membrane systems have the following possible advantages over some traditional methods:

(1) Save energy.
(2) Reduce cost.
(3) Reduce solvent consumption.
(4) Produce very high concentrated solution from dilute solution.

This section provides the economic comparison of uranium recovery by an emulsion liquid membrane system and the method current in practice.

In pretreatment, ELM requires no soluble organic removal or cooling, while SX may require some of these steps. In extraction, there is a maximum of three ELM stages versus eight SX stages for extraction and stripping. ELM, however, requires a separate coalescer and emulsifier-offsetting to some extent the capital cost savings associated with the elimination of the stripping stages. The secondary solvent step is identical for both processes.

Table (3) shows the operating costs for the extraction facilities expressed in dollars per pound of uranium recovered. One of the major differences between the ELM and SX costs are associated with organic make-up. The main differences between emulsion liquid membranes and solvent extraction are shown in Table 4. In pretreatment, ELM requires no soluble organic removal or cooling, while SX may require some of these steps. In extraction, there is a maximum of three ELM stages versus eight SX stages for extraction and stripping. ELM, however, requires a separate coalescer and emulsifier-offsetting to some extent the capital cost savings associated with the elimination of the stripping stages. The secondary solvent step is identical for both processes.

Table. 3 Capital Cost Estimates (Basis: 400,000 tons/yr Acid Capacity, 350,000 lbs/yr U_3O_8 Recovery, 2nd Qtr 1979)

	Dollar per lb of U_3O_8		
		SX	
	ELM	Minimum Pretreatment	Extensive Pretreatment
Organic make-up			
Circulation loss	0.1	3.9	3.9
Raffinate loss	0.1	0.2	0.2

Crud loss and treatment	1.0	2.9	0.0
Chemical & Supplies	1.4	0.9	1.6
Utilities	0.7	0.9	1.0
Labor, maintenance tax, & insurance	7.1	7.1	8.6
Depreciation	4.6	4.7	5.6
Total operation cost	15.0	20.6	20.9

Table. 4 Differences between ELM and Solvent Extraction

	ELM	SX
Feed Pretreatment	Oxidation Solid removal	Oxidation Solid removal Cooling Soluble organic removal
Extraction/stripping	Max. 3 stages Coalescer Emulsifier	Eight stages
Secondary extraction	Identical for both	
D_2EHPA/TOPO conc.	1/5	1
Crud make	1/4 – 1/5	1
Feed/organic ratio	18:1	1:1

CONCLUSION

The agreements of the theoretical predictions for the uranium extraction, molybdenum extraction and solvent extraction with experimental data are very good. A very important contribution of this research is that it can predict the extraction rate of an emulsion liquid membrane system without the need of experimental extraction run.

Span 80 is added to membrane phase to stabilize the emulsion and to reduce membrane breakage. From some experiments taken from the literature, at 5%v Span 80, the leakage rate was below 1%. In practical applications, the leakage problem can be neglected. Too high surfactant concentration should be avoided. Since too much surfactant in membrane phase would cause some problems in breaking up the emulsion in a subsequent process.

When chemical reaction is involved in the receiving phase, increase the receiving phase reagent concentration will also increase the extraction rate. Since the membrane rupture problem exists, the receiving phase reagent concentration cannot be too high.

From the comparison of the models with experimental data, it was concluded that for practical purpose, the internal film resistance is negligible and the external film resistance cannot be neglected. The models developed in this research are for batch process, but they can easily be modified for a continuous process. The ELM technology appears to have sufficient return on capital at today's uranium prices to warrant extraction from phosphoric acid plants.

AKNOWLEGMENT

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REFERENCES

Bird, R.B., Stewart, W.E., Lightfoot, E.N., 1960, *Transport Phenomena,* pp. 495 – 515, 594 – 619, John Wiley & Sons, Inc. New York.

LIST OF SYMBOL

a : interphase area of membrane and internal phases per unit volume of emulsion phase
a_A, a_B, a_C : as defined by eqn
A : moles of A in external extract phase
A_0 : moles of A in extract phase at time t_0

A_{0i} : initial moles of A in internal raffinate phase

b : parameter defined by eqn

b_A,b_B, b_C : as defined by eqn

B : moles of B in extract phase

B_0 : moles of B in extract phase at time t_0

B0i : initial moles of B in internal raffinate phase

C_A, C_B, C_C : concentration of A, B, C in membrane phase

C_{A0}, C_{B0}, C_{C0} : concentration of A, B, C in membrane phase at time t_0

C_U, C_H : concentration of (UO_2^{+2}) or (MoO_2^{+2}) and (H^+) in source phase

C_{UO}, C_{HO} : initial concentration of (UO_2^{+2}) or (MoO_2^{+2}) and (H^+) in source phase

C_{U*}, C_{H*} : concentration of (UO_2^{+2}) or (MoO_2^{+2}) and (H^+) in source phase at membrane external interphase

C_X, $C_{(RH)2}$: concentration of (UO_2R_22HR) or (MoO_2R_22HR) and $(RH)_2$ in membrane phase

C_{X*}, $C_{(RH)2*}$: concentration of (UO_2R_22HR) or (MoO_2R_22HR) and $(RH)_2$ at membrane external interphase

C_{Xi*}, $C_{(RH)2I*}$: concentration of (UO_2R_22HR) or (MoO_2R_22HR) and $(RH)_2$ at membrane internal interphase

C_{Ui}, C_{Hi} : concentration of (UO_2^{+2}) or (MoO_2^{+2}) and (H^+) in receiving phase

C_{Ui*}, C_{Hi*} : receiving phase concentration of (UO_2^{+2}) or (MoO_2^{+2}) and (H^+) at membarane internal interphase

Cuo : initial concentration of (UO_2^{+2}) or (MoO_2^{+2}) in source phase

$C_{(RH)2O}$: initial concentration of $(RH)_2$ in membrane phase

C_{HO} : initial concentration of (H^+) in source phase

C_{HOi} : initial concentration of (H^+) in receiving phase

D_{32} : Sauter mean diameter

D_A, D_B, D_C : diffusion coefficient of A, B, C in membrane phase

D_X, $D_{(RH)2}$: diffusion coefficient of (UO_2R_22HR) or (MoO_2R_22HR) and $(RH)_2$ in membrane phase

D_{eX}, $D_{e(RH)2}$: effective diffusivity of (UO_2R_22HR) or (MoO_2R_22HR) and $(RH)_2$ in emulsion phase

D_{eA}, D_{eB}, D_{eC} : effective diffusivity of A, B, C in emulsion phase

D_m : diffusivity of solute in membrane phase

d_g : average diameter of internal phase droplets

d_i : drop diameter

d_I : is the impeller diameter

d_{32} : the Sauter mean diameter

g : acceleration of gravity

i : a sampling size interval

k_i : membrane internal interphase mass transfer coefficient

k_o : membrane external interphase mass transfer coefficient

K_i : membrane internal resistance

K_o : membrane external resistance

m_A, m_B, m_C : distribution coefficient of A, B, C

M_B : molecular weight of solvent B

M_R : total number of moles per unit volume of raffinate phase

M_m : total number of moles per unit volume of membrane phase

M_t : total number of moles of extract phase

m and q : equilibrium constant
n : agitation speed
ni : number of drops in that interval
N : total number of globules in a batch
r : radial distance from globule center
R : Sauter mean radius of globules
Re : Reynolds number
Sc : Schmidt number
Sh : Sherwood number
SMD : Sauter mean diameter
t : time
T : temperature
U_T, U_{TS} : terminal velocity
V_A, V_B, V_C : molar volume of A, B, C
V_e : volume of external phase
V_i : volume of internal phase
V_m : volume of membrane phase
V_t : total volume of a batch
V_{EO} : initial volume of emulsion phase
We : Weber number (dimensionless group)
X_A, X_B, X_C : mole fraction of A, B, C in raffinate phase
X_{A0}, X_{B0}, X_{C0} : mole fraction of A, B, C at time t0
y : dimensionless radial distance
v_s : slip velocity of dispersed drops to continous phase (m/s)
VA : molar volume of solute A

Greek letters

ε : volume fraction of internal phase in emulsion phase
ϕ : volume fraction of emulsion phase in a batch
τ : dimensionless time
α : partition coefficient of molybdenum
ξ : association factor
ρ : density of the external phase
ρe : density of the fluid
η : emulsion phase viscosity
μ : viscosity of solvent
μe : viscosity of the fluid
γ : interfacial tension