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## Actinide Separations by Supported Liquid Membranes

P. R. Danesi, E. P. Horwitz, P. Rickert

Chemistry Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439, U.S.A.

and

R. Chiarizia

ENEA, TIB-CHI,CRE Casaccia
Rome, Italy

Supported liquid membranes (SLM), consisting of an organic solution of selected carbamoylmethylphosphoryl extractants absorbed on thin polypropylene microporous supports, have been studied for their ability to perform selective separation and concentration of actinide and lanthanide ions from aqueous nitrate feed solutions. A schematic description of such a membrane is shown in Figure 1. In our study flat-sheet CELGARD$^R$ 2500 and hollow-fiber ACCUREL$^R$ (I.D. = 0.172 cm, O.D. = 0.258 cm) microporous polyproplyene membrane supports have been used. The permeation of $Am^{3+}$ through single hollow-fiber membrane modules, operated in a continuously recycling mode, has been studied as a function of both the chemical composition of the system and the hydrodynamic conditions in order to obtain a detailed description of the rate controlling mechanisms of the permeation process. Solutions of n-octyl(phenyl)-N,N-diisobutylcarbamoymethylphosphine oxide (CMPO) in a 67% decalin, 33% diisopropylbenzene mixture were used as liquid membranes. Experiment. performed as function of the feed flow-rate through the lumen of the hollow-fiber SLM have shown that a maximum and constant value of the permeability coefficient of $Am^{3+}$ is reached (Figure 2) àt moderate values of the linear flow velocity ($V = 10$ ml/min, $R_e \sim 100$). From this maximum permeability coefficient value the

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thickness of the aqueous boundary layer was evaluated. This thickness ($\sim 1 \times 10^{-3}$ cm) has the same order of magnitude as the minimum thicknesses of the diffusion layers obtained in highly stirred flat-sheet SLM experiments. The experiments performed as function of the aqueous feed $NO_3^-$ concentration and CMPO membrane concentration have also shown that the removal of $Am^{3+}$ from the feed solution by hollow-fiber SLM can be quantitatively described by the previously derived equations[1]:

$$\ln \left(\frac{C}{C_o}\right) = -\frac{A}{V} P t \qquad (1)$$

$$P = \frac{K_d}{K_d \Delta_a + \Delta_o} \qquad (2)$$

where

$C$ = $Am^{3+}$ concentration at time $t$

$C_o$ = initial $Am^{3+}$ concentration

$A$ = internal area of the hollow-fiber ($cm^2$)

$V$ = total volume of the feed solution ($cm^3$)

$t$ = time (s)

$P$ = permeability coefficient (cm/s)

$K_d$ = $Am^{3+}$ distribution ratio between the aqueous feed solution and the liquid organic phase absorbed into the solid support pores

$\Delta_a$ = aqueous diffusional parameter (s/cm)

$\Delta_o$ = membrane diffusional parameter (s/cm)

By using Equation (2) we have demonstrated that the membrane permeation process is controlled by (a) the membrane diffusion of the Am-CMPO complex for $K_d$ values less than 5, and (b) by the rate of diffusion of the $Am^{3+}$ ions through the aqueous boundary layer when $K_d > 12$. Both processes are rate determining for intermediate $K_d$ values. Successively the permeation of $UO_2^{2+}$, $Am^{3+}$, $Pu^{4+}$, $Pu^{3+}$, $PuO_2^{2+}$ and Np (also in presence of reducing agents) through SLM's consisting of a 0.25 M CMPO + 0.75 M TBP solution in decalin, absorbed on both flat-sheet and hollow-fiber membranes, has been evaluted. The composition of the liquid membrane was selected on the basis of the previous liquid-liquid extraction studies described in Reference 2. In the permeation experiments different strip solutions were used. A strip solution containing HCOOH and hydroxylammonium formate proved to be effective when only Pu and Am were present in the feed solution. On the other hand, for U and Np a complexing strip solution, i.e., sodium citrate 0.5 M at pH ~7, had to be used. As feed solutions 1 to 5 M $HNO_3$ and synthetic nuclear waste solutions were used. The composition of the synthetic nuclear waste is reported in Tables I and II. The results of the permeation experiments have indicated that the permeability coefficients of $Am^{3+}$, $UO_2^{2+}$, $Pu^{4+}$, $Pu^{3+}$, $PuO_2^{2+}$, $Np^{4+}$ are in the order $Pu^{4+} \simeq PuO_2^{2+} > Am^{3+} \simeq Pu^{3+} \simeq UO_2^{2+} \simeq Np^{4+} >> NpO_2^{+}$, ranging from $1.7 \times 10^{-3}$ ($Pu^{4+}$, $PuO_2^{2+}$) to $1.3 \times 10^{-3}$ ($Pu^{3+}$, $Am^{3+}$, $UO_2^{2+}$, $Np^{4+}$) cm·s$^{-1}$. When synthetic nuclear wastes are used, the initial values of the permeability coefficients are about 40% lower than for 2 M $HNO_3$. The lower P values are probably caused by (a) the increased density and viscosity of the waste solutions which yield larger thicknesses of the aqueous boundary layers and (b) by the presence of other extractable species which lower the CMPO concentration available for the transport of the actinides species. A typical concentration vs time curve for the removal of $Am^{3+}$ from a synthetic nuclear waste is shown in Figure 3. The data indicate that good $Am^{3+}$ decontamination is achieved. As far as Np(V) is concerned considerable difference in behavior was observed between $HNO_3$ and the synthetic wastes. As expected from its low extractability into the liquid membrane, Np(V) shows very low permeability coefficients from $HNO_3$ feed solutions in absence of reducing agents. On the other hand, P values not much lower than those measured for the other actinides are obtained from synthetic liquid wastes. A possible explanation of this result could be the reduction of the nonextractable Np(V) to the extractable Np(IV) by oxalic acid catalyzed by one or more of the several metal

species present in the synthetic waste. Finally, the permeability coefficient of the actinides from synthetic waste solutions saturated with monobutyl (MBP) and dibutylphosphoric acid (DBP), was measured using SLM's containing MBP (0.1 M) and DBP (0.1 M) in addition to CMPO (0.25 M) and TBP (0.75 M). No appreciable variation of the permeability coefficients was observed.

In conclusion the work has demonstrated that actinide removal from synthetic waste solutions using both flat-sheet and hollow-fiber SLM's is a feasible chemical process at the laboratory scale level. The process is characterized by the typical features of SLM's processes, i.e.:

- Very small quantities of extractant are required.

- The potential for operations with high feed/strip volume ratios, resulting in a corresponding concentration factor of the actinides.

- Simplicity of operation compared to conventional liquid-liquid extraction contactors and separators, which should result in lower capital and operating cost.

Major obstacles to the implementation of the SLM technology to the decontamination of liquid nuclear wastes are:

- The probable low resistance of polypropylene supports to high radiation fields, which may prevent the application to high-level nuclear wastes.

- The unknown lifetime of the SLM.

- The high Na content of the separated actinide solution, resulting from the high sodium concentration of the strip solution.

Future efforts will be directed at better indentifying the nature of these problems and to their solution. In particular, further work is requested to optimize the composition of the strip solution.

## References

1.. P. R. Danesi, Solv. Ext. Ion Exch. $\underline{2}$(1), pp. 115-120 (1984). .

2. E. P. Horwitz, H. Diamond, and D. Kalina, Plutonium Chemistry, W. T. Carnall and G. Choppin, eds., ACS Symposium Series No. 216, pp. 433-450 (1983); E. P. Horwitz, H. Diamond, D. Kalina, L. Kaplan, and G. W. Mason, Proc. Int. Sol. Ex. Conf., ISEC83, Denver, CO, Aug. 26 - Sept. 2, 1983, pp. 451-452.

## Acknowledgment

Table I.

## Molar Concentration of Ions in the
## Synthetic Nuclear Waste Solution

| | |
|---|---|
| $H^+$ | 1.0 |
| $Al^{3+}$ | 0.78 |
| $Fe^{3+}$ | 0.16 |
| $Cr^{3+}$ | 0.015 |
| $Ni^{2+}$ | 0.007 |
| $Na^+$ | 0.21 |
| $SO_4^{2-}$ | 0.33 |
| $F^-$ | 0.14 |
| $NO_3^- + NO_2^-$ | Balance of anions ~3 |
| Oxalic Acid | 0.18 |

Table II.

**Molar Concentration of Fission Products in the**

**Synthetic Nuclear Waste Solution**

| | | | |
|---|---|---|---|
| Ge | $3 \times 10^{-7}$ | In | $0.5 \times 10^{-6}$ |
| As | $0.5 \times 10^{-7}$ | Sn | $2 \times 10^{-5}$ |
| Se | $0.25 \times 10^{-4}$ | Sb | $0.45 \times 10^{-5}$ |
| Br | $0.8 \times 10^{-5}$ | I | $1 \times 10^{-4}$ |
| Rb | $2 \times 10^{-4}$ | Cs | $0.8 \times 10^{-3}$ |
| Sr | $0.4 \times 10^{-3}$ | Ba | $0.6 \times 10^{-3}$ |
| Y | $2.5 \times 10^{-4}$ | La | $0.4 \times 10^{-3}$ |
| Zn | $1.8 \times 10^{-3}$ | Ce | $0.8 \times 10^{-3}$ |
| Mo | $1.6 \times 10^{-3}$ | Pr | $0.36 \times 10^{-3}$ |
| Te | $0.35 \times 10^{-3}$ | Nd | $1.25 \times 10^{-3}$ |
| Ru | $1 \times 10^{-3}$ | Pm | $0.85 \times 10^{-5}$ |
| Rh | $1.7 \times 10^{-4}$ | Sm | $0.25 \times 10^{-3}$ |
| Pd | $0.8 \times 10^{-3}$ | Eu | $0.5 \times 10^{-4}$ |
| Ag | $2.5 \times 10^{-5}$ | Gd | $0.35 \times 10^{-4}$ |
| Cd | $0.3 \times 10^{-4}$ | Tb | $0.55 \times 10^{-6}$ |

Fig. 1

| Feed | SL Membrane | Strip |
|---|---|---|
| Waste Solution | CMPO in decalin + (additive) | HCOOH 0.5$\underline{M}$ H$_2$SO$_4$ 0.1$\underline{M}$ |
| Am$^{3+}$ $\longrightarrow$ | | $\longrightarrow$ |

$$\longleftarrow 25\ \mu m \longrightarrow$$

CMPO =

$$R \diagdown P \diagup \phi \quad \underset{\|}{\overset{O}{P}} - CH_2 - \underset{\|}{\overset{O}{C}} - N \left[ CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} \right]_2$$

$R = C_8H_{17}$   or

$$CH_3(CH_2)_3 - \underset{\underset{CH_2-CH_3}{|}}{CH} - CH_2 -$$
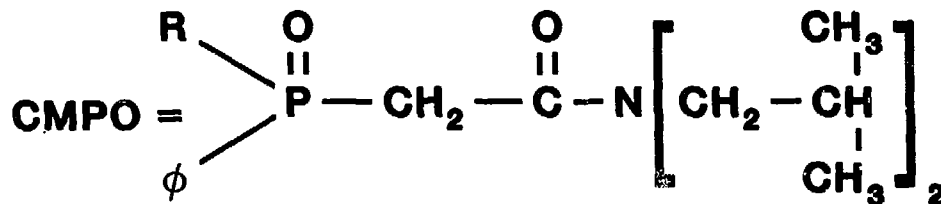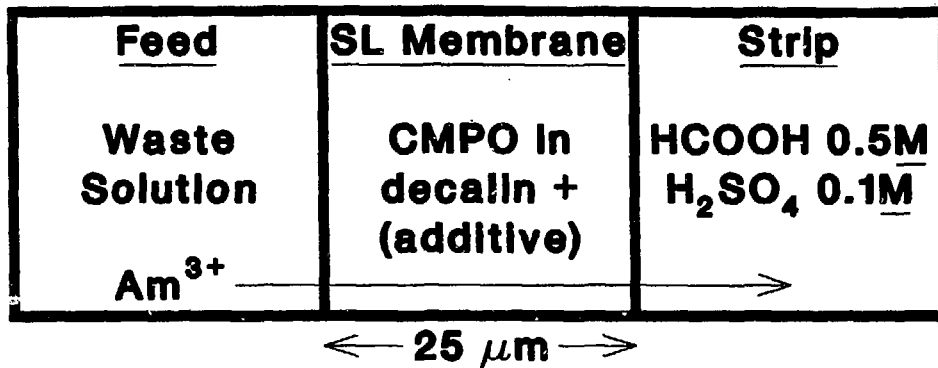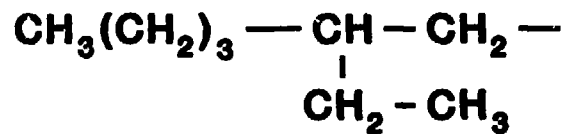
ACCUREL™ HOLLOW FIBER
$^{241}$Am TRANSPORT

Fig. 2

Fig. 3



Selective Removal of Am from Synthetic Liquid Wastes by SLM

Background

99.995% Removal

cpm $^{241}$Am

t(sec) x 10$^{-3}$

t(hrs)