Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Double Liquid Membrane System for the Removal of Actinides and Lanthanides from Acidic Nuclear Wastes

R. Chiarizia[ab]; P. R. Danesi[ac]
[a] Chemistry Division Argonne National Laboratory Argonne, Illinois [b] Visiting Scientist from E.N.E.A., Rome, Italy [c] Seibersdorf Laboratory I.A.E.A., Vienna, Austria

To cite this Article Chiarizia, R. and Danesi, P. R.(1987) 'A Double Liquid Membrane System for the Removal of Actinides and Lanthanides from Acidic Nuclear Wastes', Separation Science and Technology, 22: 2, 641 — 659
To link to this Article: DOI: 10.1080/01496398708068972
URL: http://dx.doi.org/10.1080/01496398708068972

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), 641-659, 1987

A Double Liquid Membrane System for the Removal of Actinides and Lanthanides from Acidic Nuclear Wastes

R. CHIARIZIA* and P. R. DANESI**

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439

ABSTRACT

Supported liquid membranes (SLM), consisting of an organic solution of n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and tributyl-phosphate (TBP) in decalin are able to perform selective separation and concentration of actinide and lanthanide ions from aqueous nitrate feed solutions and synthetic nuclear wastes.

In the membrane process a possible strip solution is a mixture of formic acid and hydroxylammonium formate (HAF). The effectiveness of this strip solution is reduced and eventually nullified by the simultaneous transfer through the SLM of HNO_3 which accumulates in the strip solution. A possible way to overcome this drawback is to make use of a second SLM consisting of a primary amine which is able to extract only HNO_3 from the strip solution.

In this work the results obtained by experimentally studying the membrane system: synthetic nuclear waste/CMPO-TBP membrane/HCOOH-HAF strip solution/ primary amine membrane/NaOH solution, are reported. They show that the use of a second liquid membrane is

*Visiting Scientist from E.N.E.A., Rome, Italy

**Present address:
Seibersdorf Laboratory
I.A.E.A., P. O. Box 200
A-1400, Vienna, Austria

effective in controlling the HNO_3 concentration in the strip solution, thus allowing the actinide and lanthanide ions removal from the feed solution to proceed to completion.

INTRODUCTION

In past few years Horwitz et al. (1-4) have developed the TRUEX (Transuranium Extraction) process for the removal of actinides and lanthanides from various acidic liquid nuclear wastes. The TRUEX process utilizes a n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)-tributylphosphate (TBP) solution to extract actinide and lanthanide elements. CMPO extracts lanthanide and tri-, tetra- and hexavalent actinide elements from concentrated HNO_3 solutions. The extracted cations can be stripped from the organic phase by means of dilute HNO_3. The extraction and stripping equilibria can be represented (for a trivalent cation) by the reaction

$$M^{+3} + 3NO_3^- + \overline{3\ E(HNO_3)_m} \rightleftharpoons \overline{M(NO_3)_3\ E_3(HNO_3)_n} + 3(m-n)\ HNO_3 \quad (1)$$

where E represents CMPO and the bar indicates organic species. In the presence of TBP, HNO_3 is also extracted into the organic phase according to the reaction

$$HNO_3 + \overline{TBP} \rightleftharpoons \overline{TBP\ HNO_3} \quad (2)$$

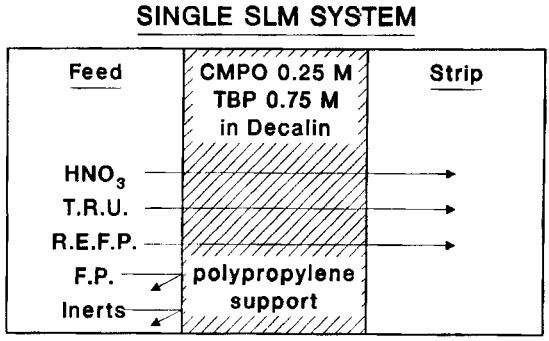
In previous work (5,6) Danesi et al. have demonstrated that supported liquid membranes (SLM) consisting of TRUEX process solvent (CMPO + TBP dissolved in decalin) absorbed on microporous polymeric supports can effectively remove and concentrate actinides and lanthanides from synthetic acidic liquid nuclear wastes to the point that the waste solutions can be considered non-transuranic (less than 100 nCi/g of disposed form) waste. A schematic description of the supported liquid membrane system is given in Fig. 1.

The previously obtained (7) equations describing the permeation rate of the actinide and lanthanide cations are:

$$\ln \frac{C}{C_o} = -\frac{A}{V} \varepsilon P t \quad (3)$$

$$P = \frac{J}{C} = \frac{K_d}{K_d \Delta_a + \Delta_o} \quad (4)$$

where C = feed concentration of metal cation at time t, C_o = feed concentration at time t=0, A = geometrical membrane area, V = volume of feed solution, ε = membrane porosity, t = permeation time, P = permeability coefficient , J = flux of the permeating species, K_d = distribution ratio of the metal species between the membrane solution and the feed solution, Δ_a = aqueous diffusional



T.R.U. = Uranium and transuranium elements

R.E.F.P. = Rare earths fission products

F.P. = Other fission products

CMPO = octyl(phenyl)-N,N diisobutylcarbamoyl methylphosphine oxide

TBP = tri-n-butylphosphate

Fig. 1. Schematic description of the single supported liquid membrane system for lanthanides and actinides removal from acidic nuclear wastes.

parameter (thickness of aqueous diffusion layer/aqueous diffusion coefficient), Δ_o = membrane diffusional parameter (thickness of membrane/membrane diffusion coefficient of the permeating species).

An important consequence of reactions (1) and (2) is that HNO_3 is also transported through the liquid membrane from the feed to the strip solution. Since the driving force for the "uphill" transport of the metal cations is provided by the concentration gradient of nitrate ions across the membrane, the build-up of NO_3^- in the strip solution continuously decreases the driving force of the transport process. Thus, after a certain length of time, which depends on the composition of the strip solution, the process eventually stops.

This behavior is shown in Fig. 2, where the americium activity in the feed solution is plotted on a semilogarithmic scale versus t. After approximately 100 minutes, the data points do not fall any longer on a straight line as predicted by equation 3.

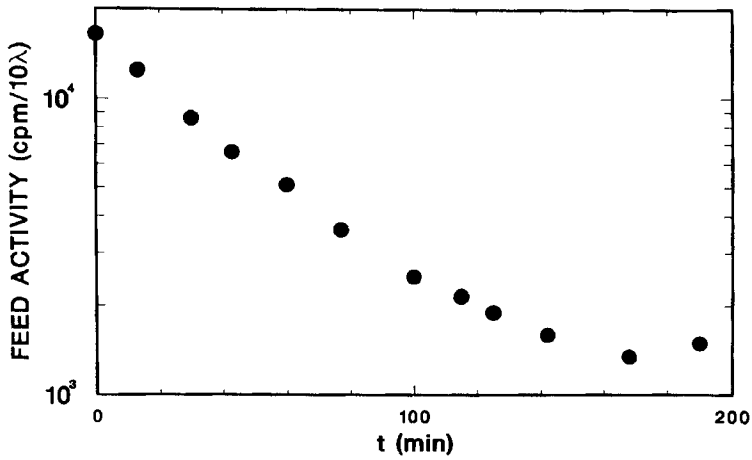


Figure 2. ^{241}Am activity (cpm/10λ) in the feed solution vs time (min). Feed = 3 M HNO_3, Strip = 1 M HCOOH. Single SLM = 0.25 M CMPO + 0.75 M TBP in decalin.

After about 150 minutes the americium transport practically stops. The consequences of this phenomenon on the choice of a suitable strip solution have been discussed at length in reference 6.

A solution containing 1 M formic acid and 0.05 M hydroxylammonium formate (HAF) is, however, a very attractive stripping solution for the following reasons:

i. it reduces Pu(IV) to the less extractable Pu(III), thus facilitating its removal from the membrane phase,
ii. HCOOH has some complexing power toward lanthanide and actinide ions (8). The formation of complexes in the aqueous stripping solution also helps in removing extracted metal cations from the membrane phase,
iii. a solution containing 1 M HCOOH has sufficient complexing ability to prevent hydrolysis of ions such as Pu(IV),
iv. the lanthanide and actinide ions can be easily recovered from the formic strip solution for re-use or vitrification. Also, the destruction of HCOOH does not increase the salt content of the final product.

A possible way to overcome the NO_3^- build-up in the formic strip solution is to circulate it in a suitable unit where a continuous destruction of nitrate ions takes place according to the reaction

$$HNO_3 + 3/2\ HCOOH \xrightarrow{>90^0C} NO + 3/2\ CO_2 + 2\ H_2O\ . \qquad (5)$$

This denitration process has been proposed and investigated (10) in order to reduce the HNO_3 concentration from ~8 M to < 1 M in feed solutions prior to ion exchange separation of transplutonium elements. Nevertheless, it is doubtful that a HNO_3 concentration as low as 0.05 M, which is required to have an efficient stripping power for the liquid membrane process shown in Figure 1, can be easily reached and controlled by means of reaction (5).

In reference 6 the possibility of using a different and entirely new way to control the nitrate concentration in the stripping solution was preliminarily mentioned. This new procedure utilizes a second liquid membrane containing a basic carrier which is capable of selectively removing HNO_3 from the stripping solution, confining it in a third aqueous compartment containing a concentrated base. As a carrier for HNO_3 removal from the stripping solution, the primary amine Primene JM-T can be used, taking advantage of the fact (11) that primary amines are very poor extractants of metal species. The use of Primene JM-T as a possible carrier for deacidification processes by means of a liquid membrane when the simultaneous removal of metal species is not desired, has been already suggested in reference 12, where the permeability of HNO_3 through membranes containing Primene JM-T dissolved in diethylbenzene was determined.

Objective of the present work was to investigate the use of a Primene JM-T liquid membrane as a way of controlling the HNO_3 concentration in the strip solution thus allowing the transport of metal species to proceed to completion.

EXPERIMENTAL

Reagents

CMPO, TBP, decalin, and all other reagents used throughout this work were the same as described previously (6). The radionuclides ^{241}Am, ^{239}Pu, ^{242}Pu, ^{237}Np, ^{99}Tc were obtained from ANL stocks and purified, where necessary, using standard procedures. Primene JM-T (Rohm and Haas Co.), a long chain primary amine, consisting of a mixture of $t\text{-}C_{18}H_{37}NH_2$ and $t\text{-}C_{22}H_{45}NH_2$, has a pK_b of 9.76 (13). The pK_a of the nitrate salt of Primene JM-T was determined by potentiometric biphasic titrations of a 1 M Primene JM-T solution in decalin with HNO_3, according to the reaction

$$\overline{RNH_2HNO_3} \overset{K_a}{\rightleftharpoons} \overline{RNH_2} + H^+ + NO_3^-\ .$$

Making use of the relation $pK_a = 2$ pH (50% titration) a pK_a value equal to 15 ± 1 was obtained.

Membranes:

Celgard 2500 (Celanese Plastic, Charlotte, North Carolina) flat sheet, 25 μm thick, 45% porosity membranes were used as a microporous polypropylene support for the TRUEX process solvent (0.25 M CMPO + 0.75 M TBP in decalin).

Feed Solutions:

The permeation experiments involving actinides were performed with the following feed solutions:

a. AW, synthetic acid waste,
b. DSW, synthetic dissolved sludge waste.

Their composition is reported in Tables 1a and 1b. Their preparation, and the rationale behind their choice to represent actual nuclear wastes are reported in references 1, 2, and 6.

Membrane Permeation Experiments

The permeation experiments were performed at 25°C utilizing different cells. In a series of experiments to determine quantitatively HNO_3 transport through single liquid membranes (containing either CMPO + TBP in decalin, SLM 1, or Primene JM-T in decalin, SLM 2) a cell identical to the one reported in Reference 14 was utilized. The membrane area was 18 cm^2, the volume of the aqueous solutions was 150 cm^3, and the stirring rate was 600 rpm.

Another series of experiments involving the measurement of HNO_3 transport was performed by using a similar cell with three aqueous compartments, where both SLM 1 and SLM 2 were used in series. A schematic description of the double SLM system is shown in Fig. 3. In these experiments $V_1 = V_2 = V_3 = 150$ cm^3, $A_2 = 18$ cm^2. A_1 could be varied by use of teflon gaskets with different openings. The stirring rate of Feed and Strip 2 solutions was 600 rpm. Strip 1 solution was stirred magnetically.

A miniaturized version of the three-compartment cell was used for the HNO_3 transport experiments both in the presence and in the absence of radionuclides. In this case, $A_1 = A_2 = 1.71$ cm^2, $V_1 = V_3 = 4$ cm^3, $V_2 = 10$ cm^2. The stirring speed was 200 rpm for Feed and Strip 2; (Strip 1 was stirred magnetically). The permeation of the radionuclides through the SLM's was measured by periodically sampling the aqueous solutions and counting the samples by either gamma (Beckmann-Biogamma II) or by liquid scintillation (Beckmann LS-100C) techniques. When the transport of HNO_3 through a single or double liquid membrane system was studied, a glass electrode Sargent-Welch S-30070-10 was used

TABLE 1a.

Composition of Synthetic Nuclear Wastes: Non Fission Products and Actinides (molar concentrations)

	AW	DSW
HNO_3	0.95	1.0
H_2SO_4	0.33	1.2×10^{-2}
NO_2^-	5×10^{-3}	5×10^{-3}
F^-	0.14	8×10^{-3}
$H_2C_2O_4$	0.18	0.3
Fe	0.16	0.15
Cr	1.5×10^{-2}	1.4×10^{-2}
Ni	7×10^{-3}	8×10^{-3}
Al	0.78	4.6×10^{-2}
Na	0.21	0.15
Ca	—	1.4×10^{-3}
Mg	—	1.6×10^{-3}
Mn	—	4.5×10^{-3}
Cu	—	1.8×10^{-3}
U+Pu+Np+Am	5×10^{-4}	5×10^{-4}

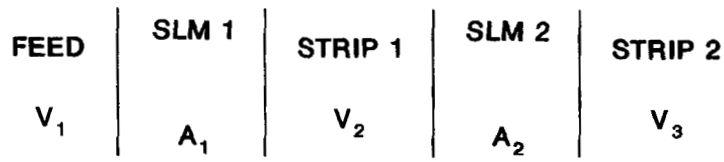


Figure 3. Schematic description of the double supported liquid membrane system investigated in this work:
SLM 1 = 0.25 M CMPO + 0.75 M TBP in decalin. SLM area = A_1.
SLM 2 = Primene JM-T in decalin. SLM area = A_2. V_1, V_2, V_3 = volumes of the Feed, Strip 1 and Strip 2 solutions, respectively.

TABLE 1b.
Composition of Synthetic Nuclear Wastes: Fission Products
(molar concentrations)

	AW	DSW
Ge	3×10^{-7}	--
As	0.5×10^{-7}	--
Se	0.25×10^{-7}	9.5×10^{-5}
Br	0.8×10^{-5}	--
Rb	2×10^{-4}	--
Sr	0.4×10^{-3}	1.4×10^{-3}
Y	2.5×10^{-4}	7.3×10^{-4}
Zr	1.8×10^{-3}	5.6×10^{-3}
Mo	1.6×10^{-3}	1.8×10^{-4}
Tc	0.35×10^{-3}	1×10^{-5}
Ru	1×10^{-3}	2.1×10^{-3}
Rh	1.7×10^{-4}	5.7×10^{-4}
Pd	0.8×10^{-3}	5.4×10^{-4}
Ag	2.5×10^{-5}	3.6×10^{-5}
Cd	0.3×10^{-4}	5×10^{-5}
In	0.5×10^{-6}	--
Sn	2×10^{-5}	--
Sb	0.45×10^{-5}	--
I	1×10^{-4}	--
Cs	0.8×10^{-3}	--
Ba	0.6×10^{-3}	1.1×10^{-3}
La	0.4×10^{-3}	1×10^{-3}
Ce	0.8×10^{-3}	2.4×10^{-3}
Pr	0.36×10^{-3}	9.2×10^{-4}
Nd	1.25×10^{-3}	2.7×10^{-3}
Pm	0.85×10^{-5}	--
Sm	0.25×10^{-3}	3.9×10^{-4}
Eu	0.5×10^{-4}	4.8×10^{-5}
Gd	0.35×10^{-4}	1.2×10^{-5}
Tb	0.55×10^{-6}	--
Te	2.00×10^{-4}	3.3×10^{-4}

together with a Fisher selective Ion Analyzer mod. 750. The same equipment was used for the biphasic titration of the Primene JM-T solutions in decalin.

The concentration variations of the nonradioactive materials present in the synthetic nuclear wastes were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

Preliminary Experiments

In a double liquid membrane system (Fig. 3), HNO_3 is transported by SLM 1 from the feed solution to Strip 1 solution, and by SLM 2 from the Strip 1 to the Strip 2 solution. Whether or not there is an accumulation of HNO_3 in the central compartment depends on the relative rates of the two transport processes. These in turn depend on the chemical composition of the various phases, on the affinity of the two liquid membranes for HNO_3, on geometrical parameters (membrane areas and phase volumes) and on the stirring rates.

In our case the feed acidity (~ 1 M) and SLM 1 composition (TRUEX process solvent) were not changed. The stirring rates were also kept constant. The only adjustable parameters were the composition of SLM 2 and the membrane areas. Our goal is to keep the HNO_3 concentration in Strip 1 always low enough to permit the continuous removal of actinide species by SLM 1. The highest acceptable concentration of HNO_3 in Strip 1 is about 0.05 M.

Preliminary experiments were performed with a large three compartment cell ($V_1 = V_2 = V_3 = 150$ cc), with the purpose of identifying the optimum experimental conditions to keep the HNO_3 concentration in Strip 1 low enough for sufficiently long times. The results are shown in Fig. 4 for different sets of experimental conditions. It appears that when the Primene JM-T concentration is 1 M, (condition 2) the HNO_3 concentration is very low even after 8 hours. A similar result is obtained when the Primene concentration is 0.2 M, and the area of SLM 1 is 2.3 cm^2 (condition 3). An even lower value of the HNO_3 concentration in the Strip 1 solution is reached in experiments 4 and 5. The data of Figure 4 indicate that for a 1 M HNO_3 feed solution, the HNO_3 concentration in Strip 1 can be effectively controlled at a steady state value lower than 0.05 M with SLM's having the same area ($\frac{\varepsilon A_1}{V_1} = \frac{\varepsilon A_2}{V_2} = 0.054\ cm^{-1}$) and with a 1 M Primene JM-T solution in the SLM 2.

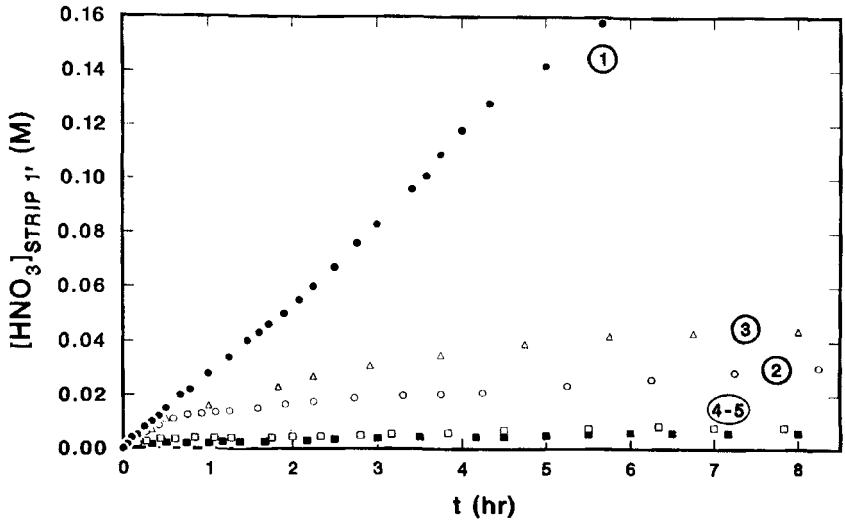


Figure 4. $[HNO_3]_{Strip1}$ vs t(hr) for the double supported liquid membrane system of Fig. 3. SLM 1 = 0.25 M CMPO + 0.75 M TBP in decalin. Strip 1 = water. Strip 2 = 4 M NaOH. $V_1 = V_2 = V_3 = 150$ cm^3. $A_2 = 18$ cm^2.
1, ●, Feed = 2 M HNO_3, SLM 2 = 0.2 M Primene JM-T in decalin, $A_1 = 18$ cm^2
2, ○, Feed = 2 M HNO_3, SLM 2 = 1 M Primene JM-T in decalin, $A_1 = 18$ cm^2
3, △, Feed = 1 M HNO_3, SLM 2 = 0.2 M Primene JM-T in decalin, $A_1 = 2.3$ cm^2
4, □, Feed = 1 M HNO_3, SLM 2 = 1 M Primene JM-T in decalin, $A_1 = 18$ cm^2
5, ■, Feed = 1 M HNO_3, SLM 2 = 1 M Primene JM-T in decalin, $A_1 = 18$ cm^2.

Quantitative Description of HNO_3 Transport

For a more quantitative description of the permeation of HNO_3 through the double SLM system, the following considerations can be made on the flux of HNO_3 through the single SLM's. At the SLM 1, where the HNO_3 concentration in the feed solution is high (~ 1 M), the HNO_3 flux, J_1, is approximately

$$J_1 = \frac{([CMPO] + [TBP])}{\Delta_o} \qquad (6)$$

where ([CMPO] + [TBP]) is the total concentration of membrane carrier for the HNO_3 transport, and Δ_o is the membrane diffusional

parameter. Note that the flux of the permeating species is independent of its concentration and is represented by the time-independent ratio of Eq. (6). This situation occurs whenever the concentration of the species transported through the SLM is high enough to saturate the carrier present in the liquid membrane. Equation (6) has been verified in a number of cases of metal and acid transport through SLM's. Its derivation and validity is discussed in detail in Reference 15.

At the SLM 2, where the concentration of HNO_3 in the Strip 1 solution is always quite low, as the data of Fig. 4 show, a different situation holds. In this case Eq. (3) applies. A time-independent permeability coefficient, P_2, of HNO_3 through SLM 2 can be defined, and the HNO_3 flux, J_2, is given by

$$J_2 = P_2 \, [HNO_3]_{Strip\ 1} \tag{7}$$

The concentration variation of HNO_3 in the intermediate compartment of a double SLM cell in experimental conditions similar to those previously shown is then given by

$$\frac{d[HNO_3]_{Strip\ 1}}{dt} = \frac{([CMPO] + [TBP])}{\Delta_o} \frac{\varepsilon A_1}{V_2} + P_2 \frac{\varepsilon A_2}{V_2} [HNO_3]_{Strip\ 1} \tag{8}$$

The first term of the sum on the righthand side of Eq. (8) represents the accumulation factor due to the transport of HNO_3 into the volume V_2 by SLM 1, and the second term represents the depletion factor due to the HNO_3 removal operated by SLM 2. It follows from Eq. (8) that when $[HNO_3]_{Strip\ 1}$ is constant with time

$$\frac{([CMPO] + [TBP])}{\Delta_o} \frac{\varepsilon A_1}{V_2} = - P_2 \frac{\varepsilon A_2}{V_2} [HNO_3]_{Strip\ 1} \tag{9}$$

The value of $[HNO_3]_{Strip\ 1}$ at the steady state can be calculated if the time independent flux through SLM 1, the permeability coefficient P_2, and the geometrical factors are known.

Determination of HNO_3 Flux through SLM 1 and HNO_3 Permeability through SLM 2

The flux of HNO_3 through the SLM 1 was determined using 1 M HNO_3 as feed and water as strip solution. The results reported in Fig. 5 show that the HNO_3 transport through SLM 1 is a zero order process with respect to the HNO_3 concentration, as expected from Eq. (6), and that a J_1 flux, constant for at least 8 hours, is obtained. The slope of the solid line is 1.82×10^{-6} M s^{-1} corresponding to a constant HNO_3 flux of 3.37×10^{-8} moles cm^{-2} s^{-1}.

To determine P_2 of Eq. (7), a single SLM experiment was performed where 0.01 M HNO_3, 1 M Primene JM-T in decalin, and 0.1 M HaOH were feed, membrane and strip solution respectively. The results are reported in Fig. 6. For acidities lower than

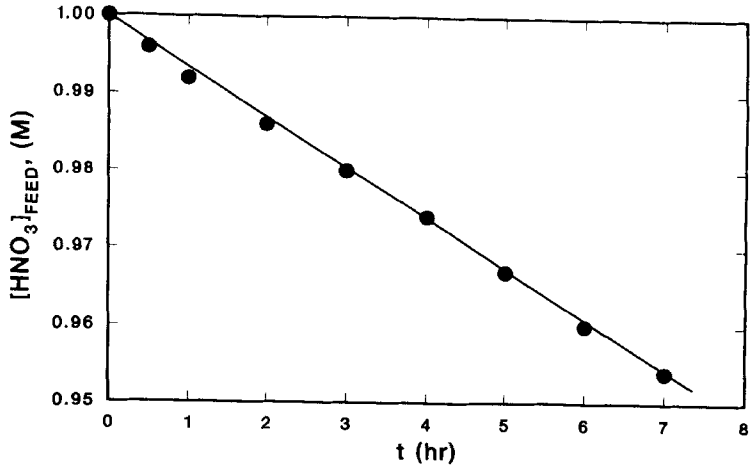


Figure 5. $[HNO_3]_{Feed}$ vs t(hr) for the single SLM 1 system. Feed = 1 M HNO_3. Strip = water. Single SLM 1 = 0.25 M CMPO + 0.75 M TBP in decalin. Volumes = 150 cm^3. Membrane area = 18 cm^2.

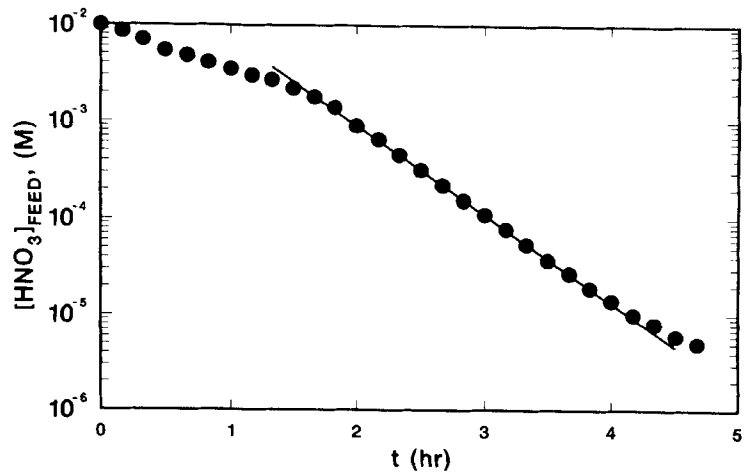


Figure 6. $[HNO_3]_{Feed}$ vs t(hr) for the single SLM 2 system. Feed = 10^{-2} M HNO_3. Strip = 0.1 M NaOH. SLM 2 = 1 M Primene JM-T in decalin. Volumes = 150 cm^3. Membrane area = 18 cm^2. The permeability coefficient P_2, calculated from the slope of the straight line is 1.1×10^{-2} $cm \cdot s^{-1}$.

$3x10^{-3}$ M, the data fall on a straight line as expected from Eq. (3). The data between $1x10^{-2}$ M and $3x10^{-3}$ M represent a transition region where neither equation (6) nor equation (7) apply. This situation has been extensively treated in Ref. 15. From the slope of the straight line passing through the experimental points the value $P_2 = 1.1x10^{-2}$ cm s^{-1} is calculated. This value is not very different from $2.1x10^{-2}$ cm s^{-1} previously reported in Ref. 12 for 0.1 M Primene JM-T in diethylbenzene.

Comparison Between Calculated and Experimental Steady State HNO_3 Concentration in Strip 1 Solution

The HNO_3 transport through the double SLM system was also studied with the same miniaturized cell used for the radionuclide transport experiments. The results of this experiment (Fig. 7) show that after an initial increase to about $4x10^{-3}$ M, the HNO_3 concentration stabilizes to a steady state value of about $2x10^{-3}$ M. This value stays constant up to at least 50 hours. The steady state HNO_3 concentration calculated by means of Eq. (9) is $3.06x10^{-3}$ M. The agreement between the experimental and calculated concentrations is reasonable, considering the approximations involved in obtaining Eq. (6) and Eq. (7). Under the experimental conditions shown in Fig. 7, the combined effect of SLM 1 and SLM 2 in controlling the HNO_3 concentration in the Strip 1 solution is therefore satisfactorily understood. The resulting HNO_3 concentration is always sufficiently low not to slow down the transport of the metal species by SLM 1.

Removal of Actinides from Synthetic Nuclear Wastes with a Double SLM System

The same three compartment cell, SLM 1, SLM 2, and Strip 2 solution have been used in a series of experiments to study the transport of actinides. In this case, the AW or DSW synthetic waste solutions and a formic acid solution (containing $5x10^{-2}$ M HAF when plutonium transport was studied) were used as Feed and Strip 1 solutions, respectively . Figure 8 reports the data obtained for the removal of americium from an AW Feed. In this case the Strip 1 solution was 1 M HCOOH. These results show that, due to the presence of SLM 2, the transport process does not stop as occurred in the experiment reported in Fig. 2. The americium permeability calculated from the data of Fig. 8 is $9x10^{-4}$ cm s^{-1} in good agreement with the results reported previously (6) obtained with only SLM 1 and sodium citrate as strip solution. Attempts to use a more diluted HCOOH solution as Strip 1 (0.1 M, HCOOH or water) were unsuccessful. The americium transport ceased after less than 1 hour probably because of the precipitation of hydrolyzed species on the strip side of the membrane.

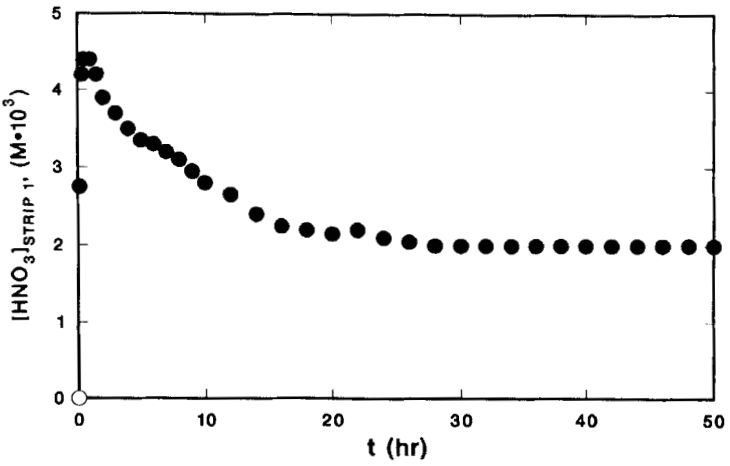


Figure 7. $[HNO_3]_{Strip\ 1}$ vs t(hr) for the double SLM system of Fig. 3. Feed = 1 M HNO_3, V_1 = 4 cm^3. SLM 1 = 0.25 M CMPO + 0.75 M TBP in decalin, A_1 = 1.71 cm^2. Strip 1 = water, V_2 = 10 cm^3. SLM 2 = 1 M Primene JM-T in decalin, A_2 = 1.71 cm^2. Strip 2 = 4 M NaOH, V_3 = 4 cm^3.

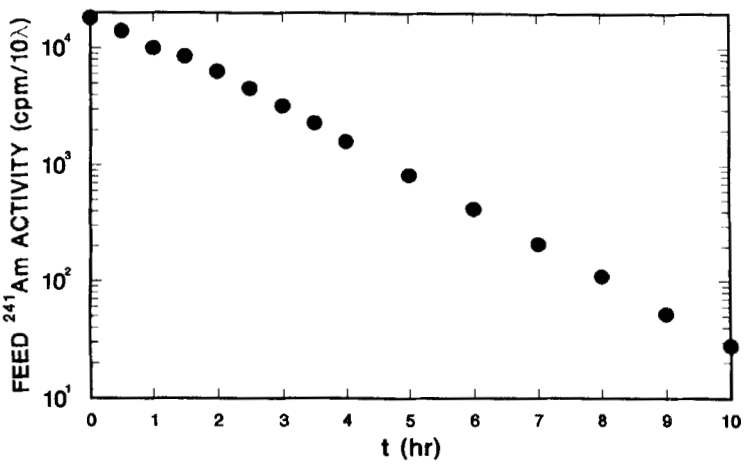


Figure 8. ^{241}Am activity (cpm/10λ) in the feed solution vs time (hr) for the double SLM system of Fig. 3. Feed = AW. Strip 1 = 1 M HCOOH. Other conditions as in Fig. 7.

Figure 9 reports a similar experiment where the AW feed was traced with plutonium. In this case also, the transport process does not slow down. The plutonium permeability coefficient is 1.0×10^{-3} cm s^{-1} in good agreement with the value cited in Ref. 6. It must be pointed out, however, that after 25 hours, when no plutonium activity could be detected in the feed solution, a small fraction of the total activity (0.76%) was found absorbed on the SLM 2 membrane. This result probably indicates that some interaction process such as polymer formation occurs at the interface between the Strip 1 solution and the SLM 2 membrane. No Pu activity was found in the Strip 2 solution.

An experiment designed to demonstrate that the total activity of a synthetic waste could be removed by a double SLM system was also performed using a DSW feed containing ^{241}Am, ^{242}Pu, ^{237}Np (10^{-4} M) and ^{99}Tc. The results of these experiments are reported in Fig. 10. The data show that it is possible to remove activity from a DSW solution yielding a waste containing less than 100 nCi of total radionuclides per gram of solidified waste utilizing a 1 M HCOOH + 5.10^{-2} M HAF stripping solution; no complications are introduced by the simultaneous HNO_3 transport. At the end of the experiment, the Strip 2 solutions contained most of ^{99}Tc. The proposed double SLM system can be then also used to selectively recover ^{99}Tc from the waste solutions.

A blank experiment identical to the one reported in Fig. 10 but with no radionuclides was also performed in order to follow the transport through the double SLM system of the DSW components which show some extractability by the TRUEX process solvent. The results are reported in Table 1 as percentage of the initial DSW components found in each compartment after 24 hours. The analyses were performed by ICP-AES with the exception of uranium which was determined by fluorescence. As expected, almost 100% of the lanthanide elements, which are extracted by the TRUEX process solvent, were found in the Strip 1 solution, together with most of the uranium, substantial quantities of yttrium and palladium and minor quantities of ruthenium, zirconium, iron, and aluminum. Only about 13% of the uranium and 6% of the ruthenium were found in the NaOH Strip 2 solution. The technetium, if present, would be then followed by minor quantities of these two elements. From the data of Table 1, it can also be seen that a good mass balance is found for all the investigated elements except for Mo, Rh, Pd, and to a lesser degree for Ru. The possibility that these latter elements precipitate partially on the SLM 2 surface or are to some extent irreversibly extracted by SLM 2 cannot be excluded. It is important to observe that HCOOH is very little extracted by the SLM 2. At the end of the experiment the Strip 1 solution was titrated and its acidity (HCOOH + HNO_3) was 0.854 M. Since we know that in these conditions the HNO_3 concentration in Strip 1 is about 2×10^{-3} M, we can conclude that only about 15% of the initial formic acid was transported into the NaOH compartment.

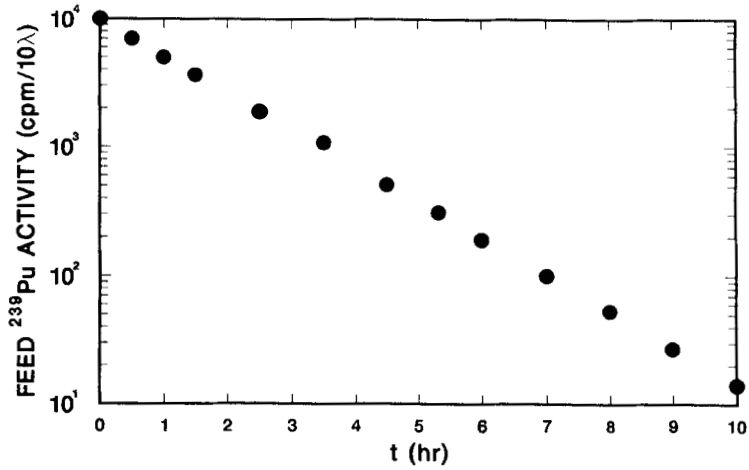


Figure 9. ^{239}Pu activity (cpm/10λ) in the feed solution vs time (hr) for the double SLM system of Fig. 3. Feed = AW. Strip 1 = 1 M HCOOH + 5×10^{-2} M HAF. Other conditions as in Fig. 7.

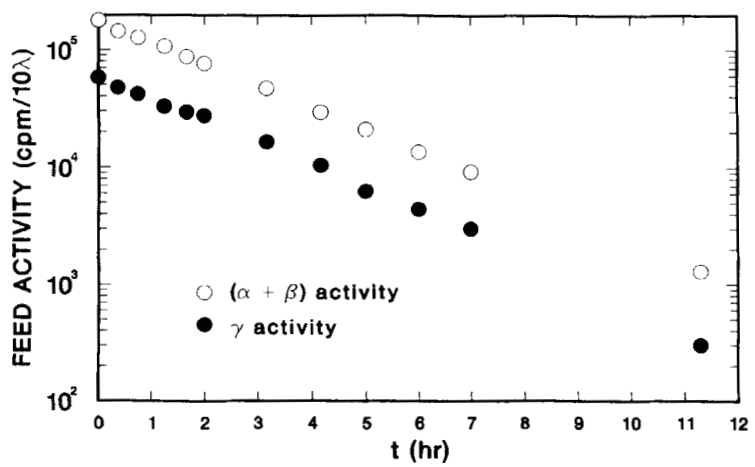


Figure 10. Total α+β (open circles) and γ (full circles) activity (cpm/10λ) in the feed solution vs time (hr) for the double SLM system of Fig. 3. Feed = DSW containing ^{241}Am (1.3×10^{7} dpm/ml ≃ 7×10^{-6} M), ^{242}Pu(3.3×10^{3} dpm/ml ≃ 2×10^{-5} M), ^{237}Np (3.7×10^{4} dpm/ml ≃ 1×10^{-4} M), ^{238}U (2.0×10^{1} dpm/ml ≃ 1×10^{-4} M), ^{99}Tc (3.7×10^{4} dpm/ml ≃ 1×10^{-5} M). Strip 1 = 1 M HCOOH + 5×10^{-2} M HAF. Other conditions as in Fig. 7.

Table 2

Concentration of Major Inactive DSW Components in a Double SLM System After 24 Hour Operation

Conditions:

Feed	SLM 1	Strip 1	SLM 2	Strip 2
V_1	A_1	V_2	A_2	V_3

Feed = DSW, V_1 = 4 cm^3

SLM 1 = 0.25 M CMPO + 0.75 M TBP in decalin, A_1 = 1.71 cm^2

Strip 1 = 1 M HCOOH + $5x10^{-2}$ M HAF, V_2 = 10 cm^3

SLM 2 = 1 M Primene JM-T in decalin, A_2 = 1.71 cm^2

Strip 2 = 4 M NaOH, V_3 = 4 cm^3

Element	Initial Molar Concentration in DSW	Feed %	Strip 1 %	Strip 2 %	Balance %
La	$1.0x10^{-3}$	2.5	97.5	0	100.0
Ce	$2.4x10^{-3}$	2.0	98.0	0	100.0
Nd	$2.7x10^{-3}$	1.0	99.0	0	100.0
Y	$7.3x10^{-4}$	30.4	69.4	0	99.8
Fe	$1.5x10^{-1}$	97.4	2.8	0.01	100.2
Al	$4.6x10^{-2}$	99.1	0.9	0	100.0
Sr	$1.4x10^{-3}$	99.2	0	0	99.2
Zr	$5.6x10^{-3}$	96.1	3.7	0.2	100.0
Mo	$1.8x10^{-4}$	88.9	0	0	88.9
Ru	$2.1x10^{-3}$	75.7	15.3	6.0	97.0
Pd	$5.4x10^{-4}$	58.6	33.9	0	92.5
Rh	$5.7x10^{-4}$	91.6	0	0	91.6
U	$1.2x10^{-4}$	1.0	85.7	13.3	100.0

Promising results were also obtained as far as the total salt content of the Strip 1 solution was concerned. The salt content of the Strip 1 solution, expressed as grams of oxides per liter of solution, was about 2, while in the initial DSW feed solution it was 230 (HNO_3 is considered neutralized as $NaNO_3$). In the experiment of Table 1 the salt content of the solution to be eventually vitrified (Strip 1) was then reduced more than 100 times.

SUMMARY AND CONCLUSIONS

The work performed has demonstrated that the problem created by the simultaneous permeation of HNO_3 together with lanthanides and actinides in a TRUEX process solvent-based SLM process for the removal of actinides from synthetic nuclear acidic wastes can be solved. The method proposed and investigated consists in contacting the stripping solution to be denitrated with a second SLM containing the carrier Primene JM-T. The primary amine selectively transports the HNO_3 to an alkaline solution where it is neutralized. The conditions to perform such a process on a laboratory scale with flat-sheet membrane supports have been worked out, and a quantitative description of the HNO_3 transport through the double SLM system has been given.

Experiments performed with synthetic waste solutions containing different radionuclides have shown that it is possible to remove the actinides, confining them in a formic acid solution. In this way periodical replacements of the strip solution or the thermal destruction of HNO_3 is avoided. Further knowledge is needed on the chemistry of the interaction at low acidity between some fission products and the Primene JM-T membrane.

ACKNOWLEDGEMENT

The authors wish to thank Dr. E. Philip Horwitz, for helpful suggestions and continuous encouragement received throughout this work, E. Huff for performing the Inductively Coupled Plasma Atomic Emission Spectroscopic Analyses of the nonradioactive components of the synthetic waste solutions, and H. Diamond for help provided in radioactivity measurements.

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract Number W-31-109-ENG-38.

REFERENCES

1. Horwitz, E. P., D. G. Kalina, H. Diamond, G. F. Vandegrift, and W. W. Schulz, Solvent Extr. Ion Exch. 3 (1,2), 75 (1985).

2. Vandegrift, G. F., R. A. Leonard, M. J. Steindler, E. P. Horwitz, L. J. Basile, H. Diamond, D. G. Kalina, and L. Kaplan, ANL-84-45, July 1984.

3. Horwitz, E. P., D. G. Kalina, H. Diamond, L. Kaplan, G. F. Vandegrift, R. A. Leonard, M. J. Steindler, W. W. Schulz, "Actinide/Lanthanide Separations," (Eds.) G. R. Choppin, J. D. Navratil, and W. W. Schulz, World Scientific Publication, Co., LTD., Republic of Singapore, 1985, p. 43.

4. Horwitz, E. P., and W. W. Schulz, "Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle," (Eds.) D. H. Logsdail and A. L. Mills, Ellis Horwood Limited, Chichester, England, 1985, p. 137.

5. Danesi, P. R., E. P. Horwitz, P. Rickert, and R. Chiarizia, Intern. Symp. on Actinide-Lanthanide Separations, ACS Intern. Congress of Pacific Basin Societies, Honolulu, Hawaii, December 16-22, 1984.

6. Danesi, P. R., R. Chiarizia, P. Rickert, and E. P. Horwitz, Solvent Extr. Ion Exch. 3 (1,2), 111 (1985).

7. Danesi, P. R., E. P. Horwitz, P. G. Rickert, J. Phys. Chem. 87, 4708 (1983).

8. Martell, A. E., and R. M. Smith, Critical Stability Constants, Vol. 3, Plenum Press, New York-London, 1977.

9. Healy, T. V., J. Appl. Chem. 8, 553 (1958).

10. Bradly, R. F., and C. B. Goodlett, DP-1299, June 1972.

11. Marcus, Y., and S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, Wiley Interscience, 1969.

12. Danesi, P. R., C. Cianetti, and E. P. Horwitz, Solvent Extr. Ion Exch. 1(2), 299 (1983).

13. Rohm and Haas Bulletin, CO-3011/1978.

14. Danesi, P. R., R. Chiarizia, and A. Castagnola, J. Memb. Sci. 14, 161 (1983).

15. Danesi, P. R., Separation Sci. and Technol. 19(11,12), 857 (1984-1985).