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Supported Extractant Membranes for Americium and Plutonium Recovery

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Supported Extractant Membranes for Americium and Plutonium Recovery

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ABSTRACT

Solid supported liquid membranes(SLM) are useful in transferring and concentrating americium and plutonium from nitrate solutions. Specifically, DHDECMP(dihexyl-N,N-diethylcarbamoylmethylphosphonate) supported on Accurel or Celgard polypropylene hollow fibers assembled in modular form transfers >95% of the americium and >70% of the plutonium from high nitrate (6.9 M), low acid (0.1 M) feeds into 0.25 M oxalic acid stripping solution. Membranes supporting TBP (tri-n-butylphosphate) also transfer these metal ions. Maximum permeabilities were observed to be 1×10^{-3} cm sec^{-1}, similar to the values for other systems. The feed:strip volume ratio shows an inverse relationship to the fraction of metal ion transferred. Cation exchangers may be used to concentrate americium from the strip solution.

INTRODUCTION

Much interest in SLM has occurred in recent years. Studies by Danesi and Horwitz and their coworkers (1,2) have defined the basic chemistry, kinetics, and operation of SLM. These systems are being examined for application to Rocky Flats Plant (RFP) nitric acid waste streams for the recovery and concentration of low concentrations (1-10 mg l^{-1}) of americium and plutonium.

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The objectives of this work are to investigate the transfer of americium and plutonium across SLM and to optimize removal and concentration factors. Two materials have been studied as liquid membranes: DHDECMP, because of its ability to extract americium from higher nitric acid concentrations(3) and TBP, an extractant for plutonium. Hollow fiber membrane supports were chosen since they exhibit the most efficient membrane area to feed volume ratio.

EXPERIMENTAL

Materials

DHDECMP was obtained as an 84 vol% pure material free from acidic contaminants from Bray Oil Co. TBP was obtained from Eastman Kodak (reagent grade). Dowex 50Wx8 resin(50-100 mesh) was obtained from Dow Chemical Co. Purified americium and plutonium were obtained from RFP production operations. All other materials were reagent grade.

Procedures

Americium and plutonium transfer behavior was studied using laboratory-built hollow-fiber membrane modules. Two different porous polypropylene hollow-fiber materials were used: Celanese Celgard™ and Armak Accurel™. The Celgard fibers (10 per module) were 11.5 cm long, 0.04 cm I. D., with 0.0025 cm wall thickness and 45 % void volume. The hollow fibers were potted into a glass tube with RTV™ silicone adhesive.

Because of recurring problems with leaks, the Celgard fibers were replaced with thicker Accurel fibers (2 per module), also 11.5 cm long, 0.15 cm I.D., with a 0.1 cm wall thickness and 75 % void volume. Connecting tubing sizes were also increased to minimize back-pressures. The data presented for Celgard fibers were obtained on runs with no leakage.

The gamma radioactivity of americium in the feed as a function of time was followed by an on-line NaI(Tl) gamma detector in conjunction with a Canberra Series 35 multichannel analyzer operating in the multi-scalar mode. The experimental system is shown schematically in Figure 1.

The feed and strip solutions were recirculated through the membrane module using Cole Parmer Master-Flex™ peristaltic pumps until no further change in feed americium concentration was observed. The initial and final actinide concentrations were determined radiometrically. Uncertainties in the data are estimated to be 5-10%.

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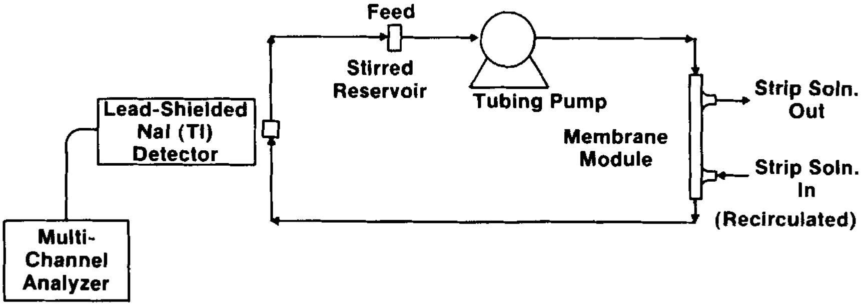

FIGURE 1

EXPERIMENTAL SET-UP OF HOLLOW FIBER MEMBRANE MODULE TRANSFER STUDY

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Permeability Calculations

Previous studies(4) have calculated the permeability (P_m) of the metal ion through the membrane from

$$\mathrm{Ln}\ \frac{[M]_o}{[M]_t} = \frac{P_m A t}{V} \qquad (1)$$

where:
$[M]_o$ = Feed concentration at time zero
$[M]_t$ = Feed concentration at time t
A = Surface area of membrane
t = Time
V = Volume of cell.

We may substitute

$$\mathrm{Ln}\ \frac{A_o}{A_t} = \frac{P_m A t}{V} \qquad (2)$$

where:
A_o = Gamma radioactivity at time zero
A_t = Gamma radioactivity at time t

since the proportionality constant between gamma radioactivity and concentration cancels out.

RESULTS AND DISCUSSION

Effect of Nitric Acid

Preliminary studies indicated incomplete transfer of americium from 7.0 M HNO_3 to 0.25 M $H_2C_2O_4$ at equilibrium through a membrane of undiluted DHDECMP. The reason for <100 % transfer is the co-transfer and build-up of nitric acid in the strip solution and consequent back-transfer of americium(5). The transfer of nitric acid was demonstrated in a separate experiment. Therefore, the transfer of americium(III) was studied as a function of nitric acid concentration at a total nitrate concentration of 7.0 M. Sodium nitrate was used to make up the balance of the nitrate. This procedure simulates a partial neutralization of a typical RFP 7.0 M HNO_3 feed stream.

Figures 2 and 3 show the results of this study plotted according to Equation (2). Figure 2 shows the results for Celgard hollow fibers with feed and strip volumes of 10 ml each, flow rates of 3 ml min^{-1}, and a net membrane area of 6.9 cm^2. Figure 3 displays those for Accurel with a feed volume of 50 ml, a strip volume of 15 ml, flow rates of 10 ml min^{-1}, and a net membrane area of 8.0 cm^2. The curves are labeled with the nitric acid concentration of the feed. The deviation from linearity at longer times indicates less than 100% transfer in all cases. Table 1 summarizes the percent americium transferred as a function of nitric acid concentration. The greatest transfer is observed at the lowest concentrations of nitric acid, as expected.

Only those experiments at 0.1 and 1.0M acidity for Celgard and only at 0.1M for Accurel have sufficient transfer to allow calculation of the permeability from a fit of Equation (2) to straight lines. These permeabilities are also summarized in Table 1. The maximum permeabilities for the Celgard fibers approach those

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TABLE 1

Percentage Transfer and Selected Permeabilities of Americium(III) through a Hollow Fiber Membrane of DHDECMP as a Function of Feed Nitric Acid Concentration
([Am] = 1.0×10^{-4} g l^{-1})

$[HNO_3]$,M	$[NaNO_3]$,M	CELGARD	P_m	ACCUREL	P_m
		%	10^{-4} cm sec^{-1}	%	10^{-4} cm sec^{-1}
7.0	0.0	47	-	61	-
5.0	2.0	55	-	64	-
3.0	4.0	76	-	76	-
2.0	5.0	87	-	-	-
1.0	6.0	97	9.6	90	-
0.1	6.9	93	8.9	94	7.2

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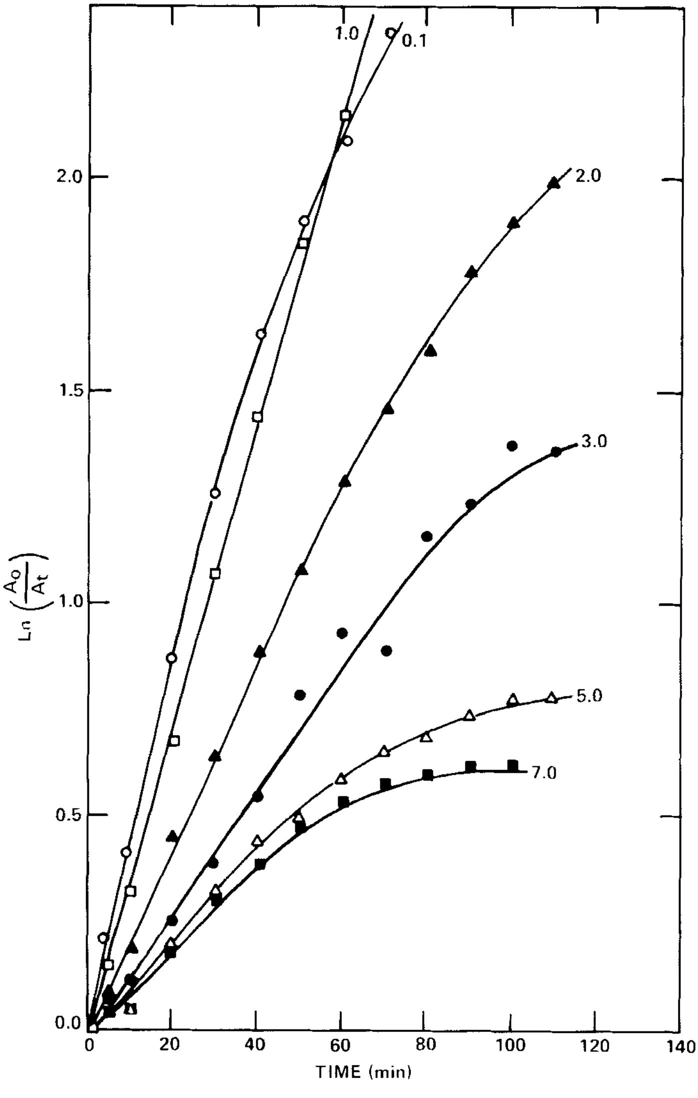

FIGURE 2. Americium transfer data for a module containing Celanese hollow fibers. A_o and A_t are gamma radioactivities at time zero and time t, respectively. The curves are labeled with the nitric acid concentration of the feed. In all cases the total nitrate concentration is 7.0M.

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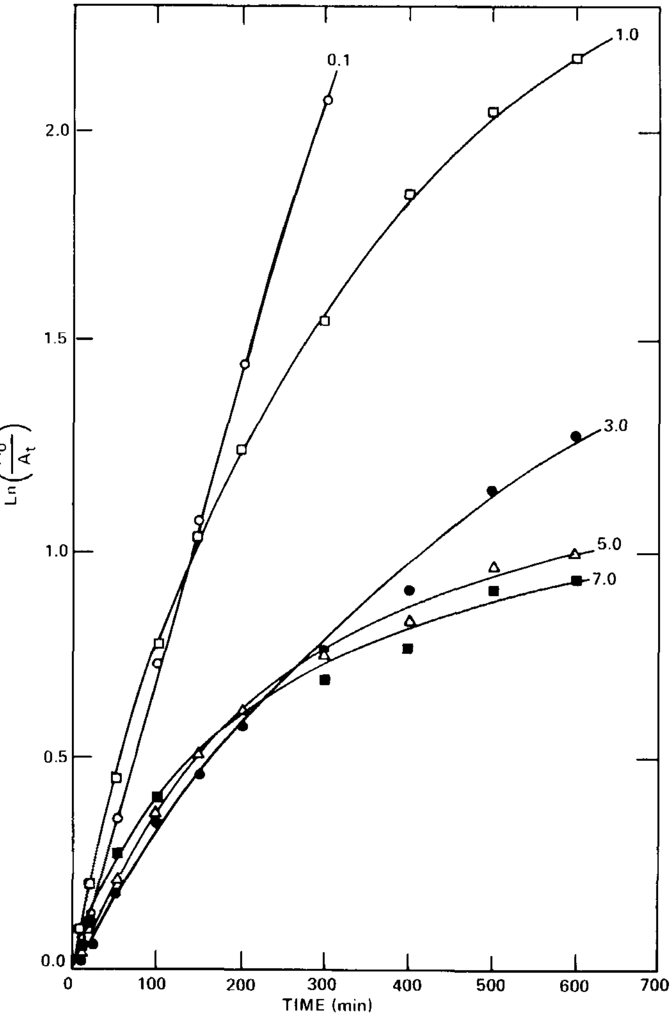

FIGURE 3. Americium transfer data for a module containing Accurel hollow fibers. A_o and A_t are the gamma radioactivities at time zero and time t, respectively. The curves are labeled with the nitric acid concentration of the feed. In all cases the total nitrate concentration is 7.0M.

determined for other metal ions in other systems using flatsheet membranes(1×10^{-3} cm sec^{-1}) (4,6). For Accurel fibers, the permeability is about twice that measured by Danesi et al.(5) in 1M HNO_3 for single hollow fiber modules, possibly because of the lower acidity and higher nitrate concentration of our experiments.

These studies indicate the best conditions of those tested for americium transfer are 0.1 M HNO_3 plus 6.9 M $NaNO_3$. Actual waste streams may be brought to these conditions by adding the correct amount of sodium hydroxide. Studies of plutonium(IV) transfer under the same conditions indicate similar permeabilities, but a lower fraction transferred (70 %).

These results are consistent with the following mechanisms (ignoring water coordination) for selective permeation, based on solvent extraction stoichiometries (3).

For americium:

Feed side:

$$Am^{3+} + 3\ NO_3^- \rightleftharpoons Am(NO_3)_3 \tag{3}$$

Membrane:

$$Am(NO_3)_3 + 3\ DHDECMP_{(0)} \rightleftharpoons Am(NO_3)_3(DHDECMP)_{3(0)} \tag{4}$$

Strip Side:

$$Am(NO_3)_3(DHDECMP)_{3(0)} \rightleftharpoons Am^{3+} + 3NO_3^- + 3\ DHDECMP_{(0)} \tag{5}$$

where a subscript (0) denotes a species in the organic phase.
For plutonium:

Feed side:

$$Pu^{4+} + 4NO_3^- \rightleftharpoons Pu(NO_3)_4 \tag{6}$$

Membrane:

$$Pu(NO_3)_4 + 2\ DHDECMP_{(0)} \rightleftharpoons Pu(NO_3)_4(DHDECMP)_{2(0)} \tag{7}$$

Strip side:

$$Pu(NO_3)_4(DHDECMP)_{2(0)} \rightleftharpoons Pu^{4+} + 4NO_3^- + 2\ DHDECMP_{(0)}. \tag{8}$$

Reactions(5) and (8) are driven to the right by the low concentration of nitrate on the strip side of the membrane and by complexation of the americium and plutonium by oxalic acid. There is also transfer of nitric acid occurring according to the reaction

$$DHDECMP_{(0)} + HNO_3 \rightleftharpoons DHDECMP \cdot HNO_{3(0)}. \tag{9}$$

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TABLE 2

Composition of Neutralized Ion Column Effluent

Component	Concentration, ppm	
Fe	21	-
Mg	5	(5)*
Ni	100	(100)
B	5	(10)
Ca	500	(100)
Cr	10	(<10)
Cu	5	(5)
Si	50	(50)
Pb	<10	(<10)
Sn	<10	(<10)

*Numbers in parentheses are the composition after transfer of Pu and Am

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Transfer by TBP

Since it is known that TBP is an extractant for americium from high nitrate-low acid solutions (7), TBP was also used as a membrane (80 volume percent in dodecane) in the Accurel module for americium transfer from 0.1 M HNO_3 plus 6.9 M $NaNO_3$. However, only 47 % of the Am(III) had transferred by equilibrium. The permeation mechanism is analogous to that of DHDECMP.

Further studies were performed using 80 vol % TBP and a simulated ion column effluent(ICE) whose composition after neutralization to 6.9 M $NaNO_3$-0.1 M HNO_3 is given in Table 2. The experimental conditions are the same as given above, except the strip was changed to 0.25 M $NaHC_2O_4$. Table 3 summarizes the results of two independent runs of the system.

The agreement in the percent transfers of both plutonium and americium is good, giving an average of 65% and 86%, respectively. These transfers show the potential of membrane transfer, and the resulting actinide concentrations in the feeds are approaching the desired limits (Am $<2 \times 10^{-5}$ g l^{-1}, Pu $< 1 \times 10^{-3}$ g l^{-1}) to give a non-TRU waste after solidification by spray drying.

Effect of Feed-to-Strip Ratio

Other experiments investigated the effect of the feed-to-strip (F:S) ratio using DHDECMP on Accurel fibers with a 7.0 M HNO_3 feed and 0.25 M $H_2C_2O_4$ strip. A roughly linear relation would be

TABLE 3

Transfer of Americium (III) and Plutonium (IV) through an 80 vol % TBP Membrane

Solution	Run #1	Run #2
Pu in Feed (g l^{-1})	$1.5x10^{-3}$	$1.4x10^{-3}$
Am in Feed (g l^{-1})	$5.4x10^{-4}$	$5.3x10^{-4}$
Pu in Depleted Feed(g l^{-1})	$4.8x10^{-4}$	$5.3x10^{-4}$
Am in Depleted Feed(g l^{-1})	$8.3x10^{-5}$	$6.2x10^{-5}$
Pu in Strip (g l^{-1})	$3.4x10^{-3}$	$8.4x10^{-4}$
Am in Strip (g l^{-1})	$1.1x10^{-3}$	$7.7x10^{-4}$
Pu Transferred (%)	68	62
Am Transferred (%)	85	89

TABLE 4

Effect of Feed:Strip Volume Ratio on the Transfer of Americium from 7.0M HNO_3 to 0.25M $H_2C_2O_4$ Through a DHDECMP SLM ([Am]=$1x10^{-3}$ g l^{-1})

Volume Ratio	% Transfer	Concentration Factor
3.3:1	80	0.90
5:1	52	0.62
10:1	45	0.58

expected between the F:S ratio and the concentration factor. However, the observed concentration factors (Table 4) are less than the F:S ratio because a large fraction of the americium remains in the membrane at the conclusion of the experiment. A roughly inverse relationship between the ratio and the percent americium transferred is observed, because of the increased concentration of nitric acid in the strip solution at higher feed:strip ratios.

Cation Exchange of the Strip Solution

Table 5 shows the results of transfer experiments at 0.1M HNO_3 plus 6.9M $NaNO_3$ feed concentrations with 0.25M oxalic acid strip concentrations where the strip solution is circulated through a small column of Dowex 50Wx8 cation exchange resin(0.87g). The

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TABLE 5

Results of the Combined Membrane/Cation Exchange System

Component (Run)	Volume ml	Initial [Am]g l^{-1}	Final [Am]g l^{-1}	Transfer %	Equilibrium Time,min
Feed (1)	75	8.0×10^{-4}	1.5×10^{-4}	82	342
Strip (1)	15	0.0	$<4.1\times10^{-6}$	-	-
Feed (2)	150	8.0×10^{-4}	1.9×10^{-4}	76	1510
Strip (2)	30	0.0	$<4.1\times10^{-6}$	-	-

cation exchange resin easily removes all the transferred americium from the strip solution, allowing a large concentration factor. The increased time for transfer in Run 2 is consistent with Equation (1) because of the increased feed volume.

Based on these results, it is possible to envision a useful membrane transfer system that removes americium from a nitrate stream and delivers it to a low acid strip solution. An inorganic cation exchange material could then be used to remove americium from the strip solution. The inorganic material would then be dried to become a safe material for long term waste storage.

SUMMARY

The planned treatment of the acid waste solutions at RFP is to remove as much of the plutonium as possible using secondary anion exchange. The effluent from anion exchange could then be reduced in acidity to 0.1M H^+ using sodium hydroxide and passed through SLM to remove additional plutonium and the americium to 1×10^{-5} g l^{-1} and 3×10^{-7} g l^{-1} levels, respectively. The effluent should then produce non-TRU waste during waste treatment operations,[8] which consist of iron hydroxide carrier precipitation.

These studies have defined some of the operating conditions for using SLM for the recovery and concentration of plutonium and americium from nitric acid feeds. DHDECMP and TBP supported on Accurel hollow fibers show promise in transferring these actinides from 6.9 M $NaNO_3$-0.1 M HNO_3 into oxalic acid strip solutions. Permeabilities of americium have been determined to be 1.0×10^{-3} cm sec^{-1}, in agreement with other membrane studies. Varying feed:strip ratios produce inverse percent americium transfer effects. Cation exchange resin can be used to give further concentration of the americium from the strip solution, and provide an excellent storage medium for the actinides. The strip solution could be recycled or sent to feed make-up.

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