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

Partitioning of Actinides from High Level Waste of PUREX Origin Using Octylphenyl-*N,N'*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO)-Based Supported Liquid Membrane

A. Ramanujam[a]; P. S. Dhami[a]; V. Gopalakrishnan[a]; N. L. Dudwadkar[a]; R. R. Chitnis[b]; J. N. Mathur[c]
[a] FUEL REPROCESSING DIVISION, BHABHA ATOMIC RESEARCH, CENTRE MUMBAI, INDIA [b] PROCESS ENGINEERING AND SYSTEMS DEVELOPMENT DIVISION, BHABHA ATOMIC RESEARCH, CENTRE MUMBAI, INDIA [c] RADIOCHEMISTRY DIVISION, BHABHA ATOMIC RESEARCH, CENTRE MUMBAI, INDIA

To cite this Article Ramanujam, A. , Dhami, P. S. , Gopalakrishnan, V. , Dudwadkar, N. L. , Chitnis, R. R. and Mathur, J. N.(1999) 'Partitioning of Actinides from High Level Waste of PUREX Origin Using Octylphenyl-*N,N'*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO)-Based Supported Liquid Membrane', Separation Science and Technology, 34: 8, 1717 — 1728
To link to this Article: DOI: 10.1080/01496399909353767
URL: http://dx.doi.org/10.1080/01496399909353767

SEPARATION SCIENCE AND TECHNOLOGY, **34**(8), pp. 1717–1728, 1999

Partitioning of Actinides from High Level Waste of PUREX Origin Using Octylphenyl-*N,N'*-diisobutylcarbamoylmethyl Phosphine Oxide (CMPO)-Based Supported Liquid Membrane

A. RAMANUJAM,* P. S. DHAMI, V. GOPALAKRISHNAN, and N. L. DUDWADKAR
FUEL REPROCESSING DIVISION

R. R. CHITNIS
PROCESS ENGINEERING AND SYSTEMS DEVELOPMENT DIVISION

J. N. MATHUR
RADIOCHEMISTRY DIVISION

BHABHA ATOMIC RESEARCH CENTRE
MUMBAI-400 085, INDIA

ABSTRACT

The present studies deal with the application of the supported liquid membrane (SLM) technique for partitioning of actinides from high level waste of PUREX origin. The process uses a solution of octylphenyl-*N,N'*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) in *n*-dodecane as a carrier with a polytetrafluoroethylene support and a mixture of citric acid, formic acid, and hydrazine hydrate as the receiving phase. The studies involve the investigation of such parameters as carrier concentration in SLM, acidity of the feed, and the feed composition. The studies indicated good transport of actinides like neptunium, americium, and plutonium across the membrane from nitric acid medium. A high concentration of uranium in the feed retards the transport of americium, suggesting the need for prior removal of uranium from the waste. The separation of actinides from uranium-lean simulated samples as well as actual high level waste has been found to be feasible using the above technique.

* To whom correspondence should be addressed.

INTRODUCTION

Alpha-emitting long-lived nuclides present in high level waste (HLW) solutions originating from the reprocessing of spent nuclear fuel are of great environmental concern. Considerable work has been carried out all over the world in the last two decades on the partitioning of actinides from acidic waste solutions by using solvent extraction (1, 2) and extraction chromatography (3). Liquid-membrane-based separation is another technique which deserves special attention because of its great potential for the separation of radionuclides, especially from waste solutions with a low metal content (4). This technique combines solvent extraction and stripping in a single step, and it has the additional advantages of lower cost and space requirements, lower energy consumption, and minimum solvent inventory, allowing the use of expensive carrier molecules.

A prime requirement for a successful liquid membrane system is the selection of a selective and efficient carrier for the species to be separated. Among various reagents used in solvent extraction and extraction chromatography, octylphenyl-*N,N'*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) has been the one most preferred in actinide partitioning because of its ability to extract tri-, tetra-, and hexavalent actinides from acidic wastes without any feed adjustment (5, 6). CMPO has been used as a carrier in the supported liquid membrane (SLM) technique for the separation of americium from nitric acid medium (4). The present studies deal with the transport of various radionuclides relevant to the PUREX process using CMPO in *n*-dodecane as a carrier. In our earlier solvent extraction studies, citric acid in the presence of formic acid and hydrazine hydrate was used for stripping actinides from acid-bearing loaded TRUEX solvent (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) (7). The buffering action of the formic acid and hydrazine hydrate mixture maintains low acid condition. Citric acid forms inextractable complexes with actinides under this condition, resulting in quantitative stripping. The same mixture is used in the present studies as a receiving phase. The transport was studied for ^{241}Am under different experimental conditions including variation in the acid content of the feed and concentration of the carrier. The studies also include the transport of other radionuclides, viz., ^{233}U, $^{237+238}$Np, and ^{239}Pu, from 3.0 M nitric acid. The studies have been extended to simulated HLW originating from the reprocessing of spent fuel from a pressurized heavy water reactor (PHWR-HLW) as well as actual HLW solutions originating from the reprocessing of spent fuel from a research reactor to test the applicability of this technique for the separation of actinides from waste solutions.

EXPERIMENTAL

Reagents

Solvent-extraction grade CMPO, which was synthesized and characterized at BARC (8), was used as the carrier. The purity of CMPO was checked by determining the distribution ratio (D) of americium using a mixture of 0.2 M CMPO and 1.2 M TBP in dodecane from 0.01 M nitric acid solution; the D_{Am} value of 0.013 suggests the absence of any significant quantities of acidic impurities in the sample (9). The purity of the purified product was also checked by IR, $^{1}H_{1}$, ^{13}C, and ^{31}P NMR spectroscopy.

Dodecane (~93% C-12, specific gravity 0.751, refractive index 1.42) was procured from M/s. Transware Chemia Handelsgeselschaft, Hamburg, Germany. All other chemicals used were of analytical reagent grade.

Materials

Commercially available polytetrafluoroethylene (PTFE) membranes were used in all the experiments. Membranes had an average pore diameter and thickness of 0.45 and 160 μm, respectively. The porosity of the membranes was about 84%. Membranes were impregnated with CMPO by immersing them in the organic phase of the required concentration for at least 12 hours before use. Impregnation of undiluted CMPO was possible in spite of its highly viscous nature at ambient temperatures (27–30°C). Single-stage transport measurements across a SLM were carried out with a two-compartment permeation cell consisting of a feed chamber and a receiver chamber (each with a volume of 4.5 mL) separated by a SLM having an effective membrane area of 1.13 cm^2. The source and receiving phases were mechanically stirred to minimize the thickness of the aqueous diffusion layer.

The transport was studied from 3.0 M nitric acid and simulated as well as with actual HLW solutions of PUREX origin. The composition of the simulated PHWR-HLW used in the present studies was based on fission product inventory of the spent uranium fuel from a pressurized heavy water reactor with a burn up of 6500 MWd/Te of UO_2 and 3 years of cooling. Inert constituents such as sodium and corrosion products like iron, chromium, and nickel were added in quantities anticipated to occur in the HLW. The composition of the simulated HLW used in the studies is shown in Table 1. The concentration of uranium in the waste was lowered to ~10 ppm by contacting it thrice with equal volumes of fresh 30% TBP in n-dodecane; the resultant raffinate was used as a feed for the experiments carried out with the simulated waste solution. A similar procedure was adopted for the removal of uranium from actual HLW generated during the reprocessing of spent fuel from a research reactor.

TABLE 1
Composition of Simulated High Level Waste Solution (acidity = 3.0 M)

Constituent	Concentration (g/L)	Constituent	Concentration (g/L)
Selenium	0.0123	Barium	0.3088
Rubidium	0.0745	Lanthanum	0.2638
Strontium	0.1863	Cerium	0.5325
Yttrium	0.0990	Praseodymium	0.2438
Zirconium	0.7713	Neodymium	0.8625
Molybdenum	0.7313	Promethium[a]	0.0283
Technetium[a]	0.1813	Samarium	0.1638
Ruthenium	0.4638	Europium	0.0226
Rhodium[a]	0.1275	Gadolinium	0.0165
Palladium	0.2675	Terbium	0.0005
Silver	0.0186	Dysprosium	0.0002
Cadmium	0.0159	Uranium	18.325
Tin	0.0151	Sodium	3.0
Antimony	0.0047	Iron	0.5
Tellurium	0.1028	Chromium	0.1
Cesium	0.5438	Nickel	0.1

[a] Lanthanum was added for promethium, molybdenum for technetium, and cobalt for rhodium.

The feed solution used in the transport studies was spiked with radiotracers like ^{233}U, $^{237+238}Np$, ^{241}Am, and ^{144}Ce according to the requirement of each experiment. The oxidation state of neptunium was adjusted to either IV or VI by using 0.02 M ferrous or 0.01 M dichromate ions, respectively, before spiking.

Analysis

In all the experiments, samples of 20 μL were taken from the feed and receiving compartments periodically and analyzed radiometrically. ^{233}U and ^{239}Pu were analyzed using an alpha proportional counter. A single channel gamma analyzer with a NaI(T1) detector was used for the analysis of ^{238}Np, ^{241}Am, and ^{144}Ce.

RESULTS AND DISCUSSION

The present system uses CMPO as a carrier for the transport of metal ions. The permeability of various species is dependent on the concentration of the carrier in the SLM. Figure 1 shows the transport of ^{241}Am from 3.0 M nitric acid through a SLM with varying concentrations of the carrier while using a

mixture of 0.1 M citric acid, 0.4 M formic acid, and 0.4 M hydrazine hydrate as the receiving phase. The transport is expressed as the percentage of the initial activity in the feed transferred to the receiving phase. When the concentration of CMPO is between 0.3 to 0.8 M, transport of ^{241}Am is found to exceed 99% in 45 minutes. However, transport is slow when the carrier concentration is increased beyond 1.2 M. With undiluted CMPO (2.95 M), nearly 36 hours were required for the quantitative transfer of ^{241}Am. The low transfer of ^{241}Am in this case was probably due to the high viscosity of the carrier phase. The low transport of ^{241}Am observed with 0.1 M CMPO in the membrane phase could be due to insufficient concentration of carrier.

Results of studies on the effect of nitric acid concentration in the feed on the transport of ^{241}Am using 0.2 M CMPO in *n*-dodecane are presented in Fig. 2. The extent of transport was found to reach nearly 100% with a mixture of 0.1 M citric acid, 0.4 M formic acid, and 0.4 M hydrazine hydrate as the receiving phase after 45 minutes for feed acidities of 1.0 and 3.0 M. Transport was slightly slower when the feed acidity was 0.5 M. Nevertheless, quantitative transfer is possible within 60 minutes. Slow transfer of ^{241}Am from feed with a low acid content is probably due to reduced extraction into the membrane phase. The transport of ^{241} Am was studied re-

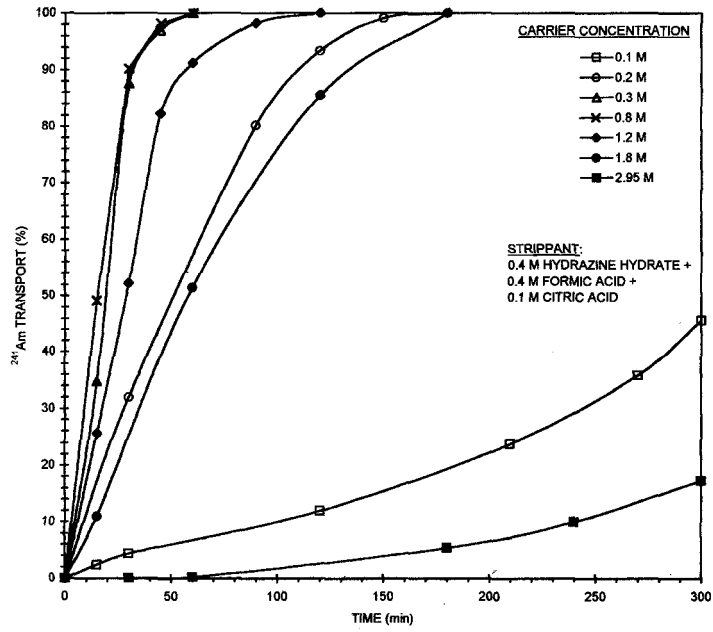

FIG. 1 Transport of ^{241}Am at various CMPO concentrations from 3.0 M nitric acid.

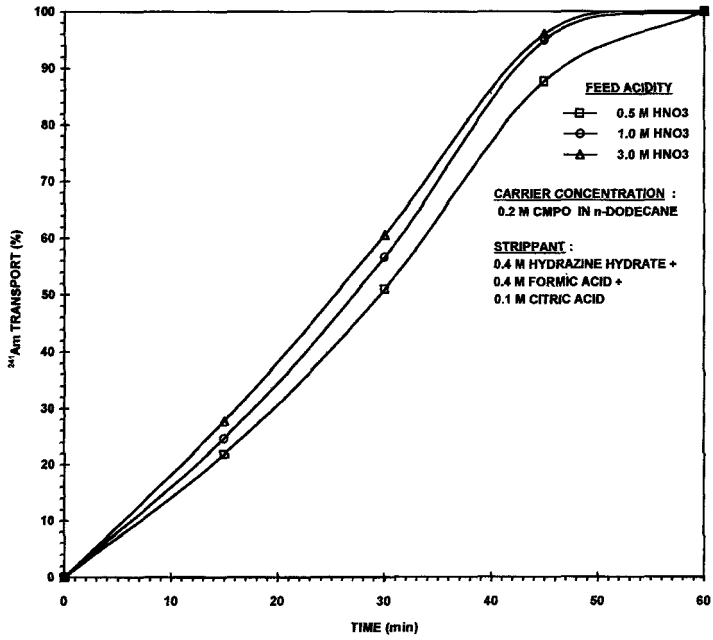

FIG. 2 Transport of ^{241}Am at various nitric acid concentrations.

peatedly from 3.0 M nitric acid solutions using the same membrane. No change in permeability was observed for the first 15 days. After 20 days the time required for quantitative transport was increased by ~5%, indicative of a carrier loss.

The transport of various metal ions, viz., U(VI), Np(IV), Np(VI), Pu(IV), Am(III), and Ce(III), was studied from 3.0 M nitric acid through a membrane containing 0.2 M CMPO in *n*-dodecane. The respective permeability coefficients were calculated by using following equation (10):

$$\ln(M_t/M_0) = -(A\epsilon/V)\,Pt$$

where M_0 is the concentration of radionuclide in the feed at time $t = 0$, M_t is the concentration of radionuclide in the feed at time t minutes, A is the geometric area of the membrane in cm^2, ϵ is the porosity, V is the volume of the feed in cm^3, P is the permeability coefficient in cm/min, and t is the lapsed time in minutes. Figure 3 shows straight line graphs for $\ln(M_t/M_0)$ vs time for different radionuclides. The permeability coefficients for each radionuclide as calculated from the slopes of the straight lines are presented in Table 2. Am(III), Ce(III), Np(IV), and Np(VI) exhibit high permeability coefficients in

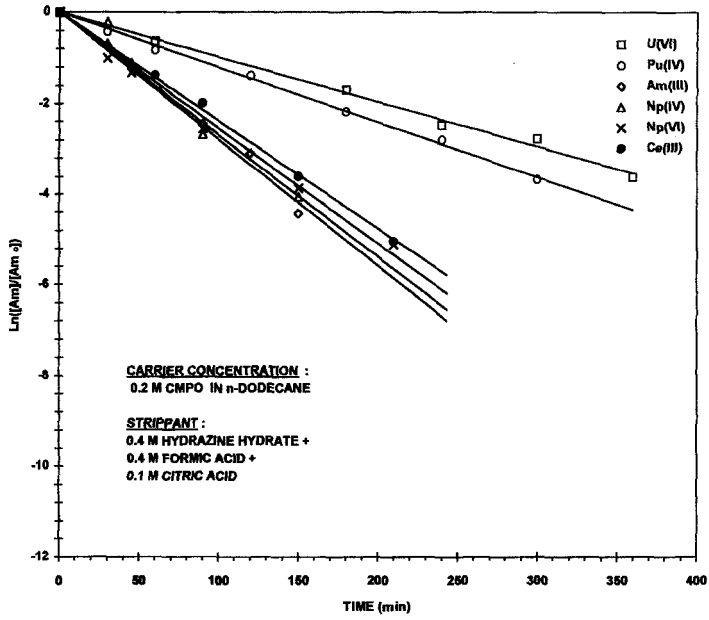

FIG. 3 Transport of different radionuclides from 3.0 M nitric acid.

the present system, while the permeability coefficients for U(VI) and Pu(IV) are relatively low. As compared to Pu(IV) and U(IV), trivalent actinides and lanthanides have a lower affinity for CMPO (11), which facilitates their permeation at the low acidity maintained in the receiver phase. However, the re-

TABLE 2
Permeability Coefficients for Different Radionuclides from 3.0 M Nitric Acid (carrier concentration: 0.2 M CMPO in *n*-dodecane. receiving phase: 0.1 M citric acid + 0.4 M formic acid + 0.4 M hydrazine hydrate)

Species	Permeability coefficients [(cm/min) × 10^3]
U(VI)	0.47
Np(IV)	1.28
Np(VI)	1.20
Pu(IV)	0.57
Am(III)	1.32
Ce(III)	1.13

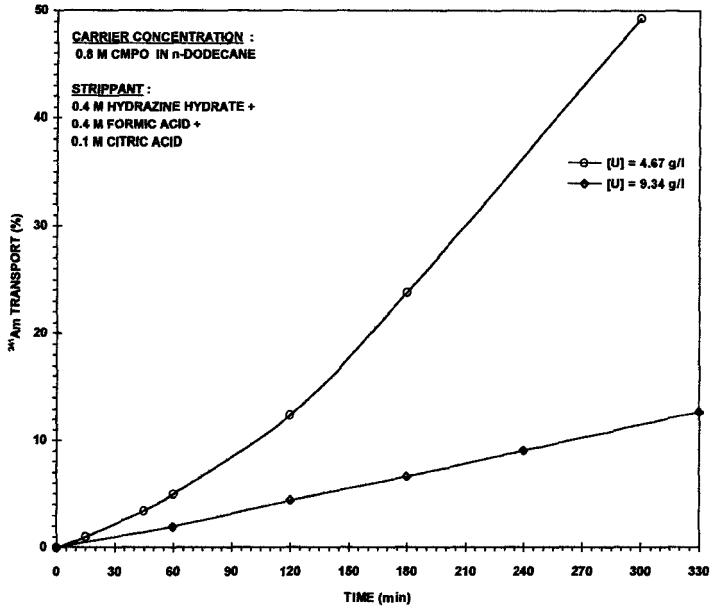

FIG. 4 Transport of ^{241}Am from 3.0 M nitric acid in the presence of uranium.

duction of Pu(IV) to Pu(III) is slow with the reagents used, which lowers the transport of Pu(IV) from the CMPO phase. The higher permeability coefficient for Np(IV) than for Pu(IV) needs to be further investigated, though it is known that Pu(IV) has a stronger affinity for CMPO than does Np(IV).

Since HLW solutions have a high uranium content, the transport of ^{241}Am was studied from 3.0 M nitric acid solution in the presence of uranium. The results of these experiments conducted with 0.8 M CMPO in *n*-dodecane as a carrier using a mixture of citric acid, formic acid, and hydrazine hydrate as a receiving phase are presented in Fig. 4. It is seen from the figure that the transport of americium slows down in the presence of uranium due to its co-transport. In the presence of 9.34 g/L of uranium, only ~13% of the americium was transported to the receiver chamber in 5 hours. In order to enhance the rate of transport of americium, it is necessary to remove uranium from the HLW prior to partitioning when using the membrane technique. The removal of uranium from the HLW can best be achieved through solvent extraction using TBP. Further experiments were carried out on uranium-lean simulated HLW.

Figure 5 shows the results of transport studies of ^{241}Am from the uranium-lean raffinate of a simulated HLW using a mixture of 0.1 M citric acid, 0.4 M formic acid, and 0.4 M hydrazine hydrate as the receiving phase. Although the

earlier experiments (Fig. 1) showed that a carrier concentration between 0.3 to 0.8 M can be used for efficient partitioning of americium from nitric acid solutions, the highest carrier concentration of 0.8 M was used for the partitioning of actinides from the waste solution to compensate for possible carrier losses. In this experiment with simulated HLW raffinate, quantitative transport of ^{241}Am occurred in 20 hours. A high content of transportable fission products in the HLW made the transport slow compared to that from a pure nitric acid feed. The time period of 20 hours required for quantitative partitioning of americium from PHWR-HLW is high compared to what is required in solvent extraction and extraction chromatographic techniques. But at the same time, the method has many advantages such as ease of operation and others mentioned earlier.

The results of the experiment with americium in 3.0 M nitric acid, using dilute nitric acid (0.04 M) as the receiving phase, are presented in Fig. 6 for comparison. Although nearly 95% of the americium was transferred to the receiving chamber in the initial stages of the experiment, subsequently americium began migrating back to the feed chamber. This reversal in the direction of the movement of americium was due to an increase in the nitric acid content of the receiving chamber resulting from co-transport of nitric acid. After 24 hours,

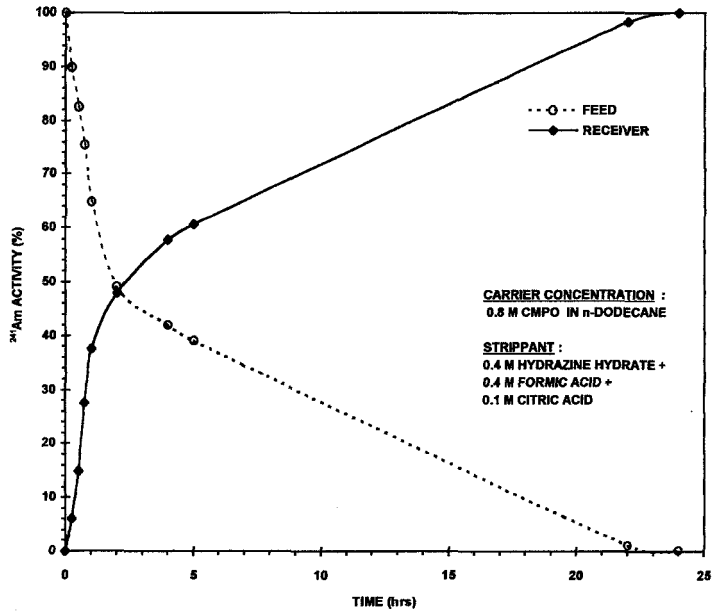

FIG. 5 Transport of ^{241}Am from uranium-lean HLW using a complexing agent.

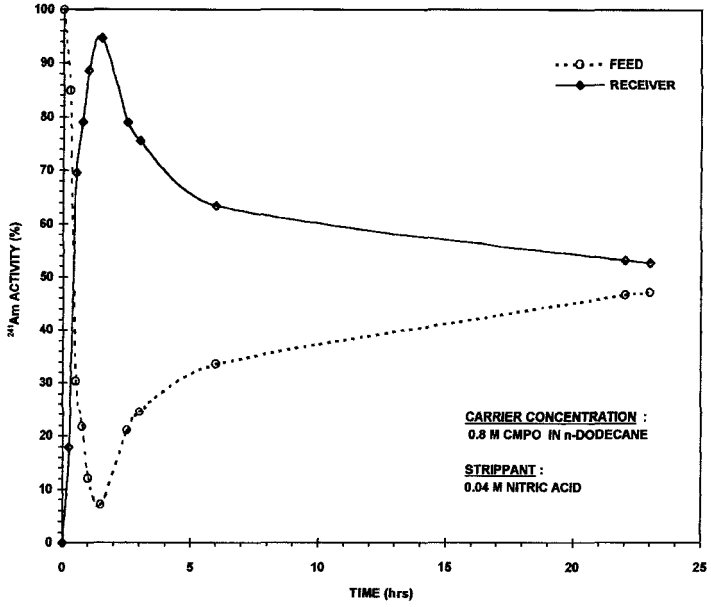

FIG. 6 Transport of ^{241}Am from uranium-lean HLW using dilute nitric acid.

americium was equally distributed in the two chambers. The initial nitric acid content of the feed was also found to be distributed equally in both chambers after 24 hours. A similar distribution of the acidity was observed when the experiment was conducted with a feed with a low acidity of 0.7 M. This behavior was not due to a breakdown of the SLM because the same membrane could be reused without any deterioration in the performance when the receiving phase was changed to the chosen buffer. In the case of a receiving phase containing formic acid and hydrazine hydrate, the buffering action against the nitric acid keeps the transport of Am(III) unhindered in spite of acid transport to the receiving phase across the membrane. The osmolality of the receiving phase also may lead to lowering the transport of nitric acid.

Figure 7 shows the results of experiments carried out on actual uranium-lean HLW from the PUREX process by using 0.8 M CMPO in *n*-dodecane as a carrier with a mixture of 0.1 M citric acid, 0.4 M formic acid, and 0.4 M hydrazine hydrate as the receiving phase. The partitioning of actinides is complete within 60 minutes as indicated by measurement of the total α-activity. The initial acid content of uranium-depleted feed is halved at the end of the experiment. The high rate of transport for actinides observed in this case com-

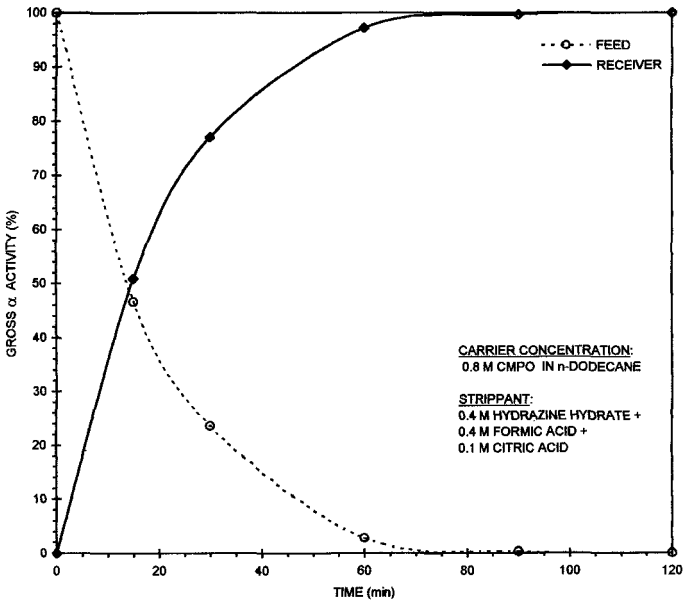

FIG. 7 Transport of gross α-activity from actual uranium-lean HLW.

pared to that of simulated PHWR-HLW is attributed to the presence of low concentrations of other transportable species.

The highly radioactive solution (activity ~ 90 Ci/L) was left in the experimental setup undisturbed for 3 more days in order to study the effect of radiation on membrane performance. After removal of the solutions, the membrane was reused to study the transport of americium from a uranium-lean simulated HLW by using a receiving phase containing citric acid, formic acid, and hydrazine hydrate. No change in transport characteristics was observed, indicating the stability of the membrane under the above experimental conditions.

CONCLUSION

CMPO-based supported liquid membranes can be employed for the partitioning of actinides from high level waste solutions. Fast separation of neptunium, plutonium, and americium can be accomplished by using a solution of CMPO in *n*-dodecane at a concentration between 0.2 to 0.8 M as the carrier and a mixture of 0.1 M citric acid, 0.4 M formic acid, and 0.4 M hydrazine hy-

drate as the receiving phase. The proposed receiving phase can be effectively used for a feed with a nitric acid content between 0.5 to 3.0 M. Since the transport rates were found to be very low in the presence of a high concentration of uranium, the present method will have its best results only after the uranium content of the waste solution is lowered.

REFERENCES

1. W. W. Schulz and E. P. Horwitz, *Sep. Sci. Technol.*, *23*, 1191 (1988).
2. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, A. Banerji, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, R. K. Dhumwad, and M. K. Rao, *Waste Manage.*, *13*, 317 (1993).
3. J. N. Mathur, M. S. Murali, R. H. Iyer, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, L. P. Badheka, and A. Banerji, *Nucl. Technol.*, *109*, 216 (1995).
4. P. R. Danesi, R. Chiarizia, P. G. Rickert, and E. P. Horwitz, *Solv. Extr. Ion Exch.*, *3*, 111 (1985).
5. E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason, and H. Diamond, *Sep. Sci. Technol.*, *17*, 1261 (1982).
6. E. P. Horwitz and D. G. Kalina, *Solv. Extr. Ion Exch.*, 2, 179 (1984).
7. R. R. Chitnis, P. K. Wattal, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, K. Bauri, and A. Banerji, *J. Radioanal. Nucl. Chem.*, In Press.
8. J. N. Mathur, M. S. Murali, P. R. Natarajan, L. P. Badheka, and A. Banerji, *Talanta*, *39*, 493 (1992).
9. R. Chiarizia and E. P. Horwitz, *Solv. Extr. Ion Exch.* 8,907 (1990)
10. P. R. Danesi, E. P. Horwitz, and P. G. Rickert, *J. Phys. Chem.*, *87*, 4708 (1983).
11. W. W. Schulz and E. P. Horwitz, *Extraction '87* (I. Chem. E. Symp. Ser. 103), 1987, p. 245.

Received by editor April 7, 1998
Revision received August 1998