Application of Supported Liquid Membranes for Removal of Uranium from Groundwater

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APPLICATION OF SUPPORTED LIQUID MEMBRANES FOR REMOVAL OF URANIUM FROM GROUNDWATER*

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ABSTRACT

The separation of uranium from Hanford site groundwater was studied by hollow-fiber supported liquid membranes, SLM. The carrier bis(2,4,4-trimethylpentyl)phosphinic acid, H[DTMPeP], contained in the commercial extractant Cyanex™ 272 was used as membrane carrier, because of its selectivity for U over calcium and magnesium.   The water soluble complexing agent, 1-hydroxyethane-1,1-diphosphonic acid, HEDPA, was used as stripping agent. Polyproylene hollow-fibers and n-dodecane were used as polymeric support and diluent, respectively. Laboratory scale hollow-fiber modules were employed in a recycling mode, using as feed synthetic groundwater at pH 2, to confirm the capability of the proposed SLM system to separate and concentrate U(VI) in the strip solution. Information was obtained on the U(VI) concentration factor and on the long-term performance of the SLMs. Encouraging results were obtained both with a conventional module and with a module containing a carrier solution reservoir. Industrial scale modules were used at Hanford to test the SLM separation of U(VI) from real contaminated groundwater.   The uranium concentration was reduced from approximately 3,500 ppb to about 1 ppb in a few hours.
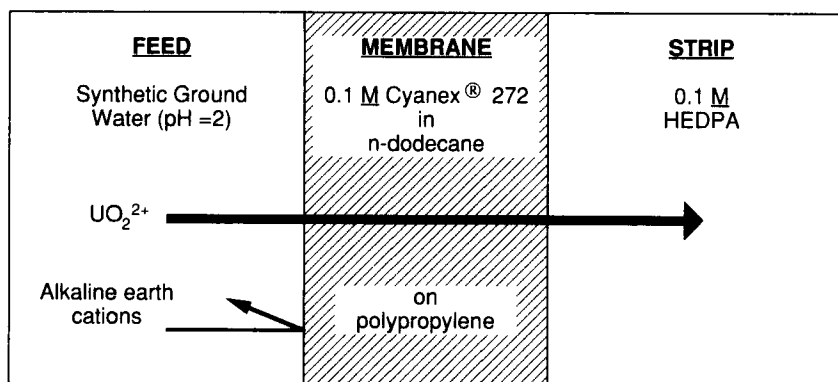
INTRODUCTION

In a previous study (1) we reported on the application of a supported liquid membrane system for the removal of uranium(VI) from contaminated groundwater. We demonstrated that the carrier bis(2,4,4-trimethylpentyl)-phosphinic acid

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(H[DTMPeP]), contained in the commercial extractant Cyanex™ 272, was very effective in removing uranium (VI) from synthetic groundwater acidified to pH 2 with sulfuric acid, and that the separated uranium could be stripped and concentrated in a solution containing 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). The SLM system is schematically shown in Fig. 1.

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Fig. 1. Schematic of SLM for the removal of U(VI) from groundwater.

The SLM study reported in ref. (1) was performed using flat-sheet polymeric supports for the membrane, because the main goal of that investigation was to establish the best chemical conditions for the desired separation. For a practical application of a SLM based separation, however, hollow-fiber polymeric supports are more effective because of their more favorable ratio of membrane area to volume of circulating solutions.

In ref. (2) Danesi demonstrated that the same equations holding for flat-sheet SLMs can be used in the case of hollow-fiber membranes operated in a recycling mode, providing the flow rate through the fibers is high enough. These equations, derived in (3), are summarized below. The permeability coefficient of the permeating species is related to distribution and diffusion parameters by

$$P = J/C = \frac{K_d}{K_d \Delta_a + \Delta_o} \tag{1}$$

with P = permeability coefficient, cm s^{-1}
   J = flux of the permeating species, $\underline{M}$ s^{-1} cm
   C = feed concentration, $\underline{M}$
   K_d = distribution ratio of the metal species between the membrane solution and the feed solution
   $\Delta_a = d_a/D_a$ = thickness of aqueous diffusion layer/aqueous diffusion coefficient, cm^{-1}s

$\Delta_o = d_o/D_{o, app}$ = membrane thickness/apparent diffusion coefficient of the permeating species in the membrane, cm^{-1} s.

The diffusional parameter Δ_a is the reciprocal mass transfer coefficient of the diffusion species in the aqueous diffusion film.

The flux is defined as:

$$J = -\frac{dC}{dt}\frac{V}{A}$$
(2)

where V is the volume of the feed solution and A the membrane area. The integration of eq. (2) leads to:

$$\ln = \frac{C}{C_o} = -\frac{A}{V} Pt$$
(3)

where C_o is the value of C at time zero.

Equations (1) and (3) are very useful for predicting the behavior of SLMs. However, to apply eqs. (1) and (3) the following limiting conditions must exist: the distribution ratio at the membrane-aqueous strip interface is much lower than at the membrane-aqueous feed interface, the interfacial chemical reactions are fast, and the concentration of the permeating species is much lower than that of the carrier (3). These limiting conditions are all met in the application of our SLM system for the uranium (VI) removal from groundwater.

In this work we have extended our investigation to the uranium (VI) transport through hollow-fiber supported liquid membranes with the following objectives:
— to verify, with small laboratory scale hollow-fiber modules, the validity of the results obtained with flat-sheet supports;
— to demonstrate that high concentration factors of U(VI) can be achieved;
— to obtain information on the long-term stability of the hollow-fiber SLMs;
— to test the developed liquid membrane system with real contaminated groundwater, using commercial hollow-fiber membrane modules.

EXPERIMENTAL

Groundwater

Several liters of synthetic Hanford site groundwater (SGW) were prepared as reported in (1). After addition of enough concentrated sulfuric acid to bring the pH value to about 2, the resultant mixture had the composition reported in Table 1. The solution simulates the composition of contaminated groundwater acidified to pH $\simeq$ 2 using sulfuric acid.

The groundwater used at Hanford was obtained from the monitoring well 2-W19-3. The expected composition of the groundwater, based on samples taken in December 1987 is given in Table 2. The uranium concentration (8,590 ppb = 3.61 $\times$ 10^{-5} $\underline{M}$) was much higher than the Maximum Contaminant Limit (10 ppb = 4.20 $\times$ 10^{-8} $\underline{M}$).

Table 1. Composition of SGW at pH ≃ 2.

Constituent	Molarity
Calcium	0.012
Magnesium	0.0062
Sodium	0.017
Silicon	0.0009
Chloride	0.0016
Sulfate-bisulfate	0.017
Nitrate	0.030
Uranium	0.0004
pH	2.09
Sum of molarities	0.094

Table 2. Analysis of Water from Well 2-W19-03.

Chemical Component	Concentrations
Barium	49 ppb
Calcium	49,900 ppb
Chloride	19,100 ppb
Copper	12 ppb
Fluoride	965 ppb
Iron	245 ppb
Magnesium	14,100 ppb
Manganese	9.0 ppb
Nitrate	93,000 ppb
pH	7.92
Potassium	4,630 ppb
Radium	0.25 pCi/L
Sodium	77,100 ppb
Specific conductance	606 umho
Strontium	207 ppb
TOXLDL[a]	69 ppb
Tri-butyl phosphate	10 ppb
Carbon tetrachloride	86 ppb
Total carbon	44,800 ppb
Total organic carbon	643 ppb
Zinc	15 ppb
Uranium	8,590 ppb
(Sampled 12/09/87)	
Total alpha	3,930 pCi/L
Total beta	4,050 pCi/L
Nitrate	71,400 ppb
Cesium-137	5.08 pCi/L
Cobalt-60	3.03 pCi/L
Technetium-99	1,860 pCi/L

[a]Toxic organic halogen-low detection limit.

Reagents

Cyanex™ 272, the membrane carrier for U(VI), was obtained from American Cyanamid Company and used as received. n-Dodecane was used as the diluent for Cyanex™ 272, because it is known to interact only slowly with the support material (4). 0.1 $\underline{M}$ Cyanex in n-dodecane was used as liquid membrane throughout this work.

1-Hydroxyethane-1,1-diphosphonic acid, HEDPA, was obtained from the Albright and Wilson Company as a concentrated aqueous solution. It was recrystallized from glacial acetic acid. A 0.1 $\underline{M}$ solution of HEDPA was used as strip solution, when not otherwise specified.

Vinylidene-1,1-diphosphonic acid, VDPA, was prepared and purified as described in (5). It was also used as stripping agent in some stability experiments.

All other reagents were analytical grade and were used without further purification.

Radioisotopes

The stock solutions of ^{233}U, ^{45}Ca, and ^{59}Fe were the same as in (1). Small aliquots of the tracer stock solutions were used, when necessary, to spike the feed solutions for the permeation experiments.

Hollow-fibers

Hollow-fiber supports were obtained from ENKA America, Inc. in the form of a MICROSTAT cartridge. The cartridge was disassembled and the hollow-fibers were used to fabricate small laboratory modules. Hollow-fiber supports, 7 to 14 cm long, containing from 4 to 100 fibers, were fabricated by inserting the desired number of fibers into a glass hollow tube having a side opening at each extreme. The fibers were sealed into the tube with an epoxy resin (5 minutes curing time). The epoxy seal extended into the tube for a few millimeters, providing complete isolation of the feed and strip aqueous solutions.

The liquid membrane was sorbed on the hollow-fibers by flowing, at a slow rate, the organic solution through the fiber lumen and then rinsing the lumen several times with distilled water to eliminate any excess of organic solution.

Table 3. Characteristics of the SLM modules used in this work.

	Homemade	Commercial
Internal surface area	9.8-245 cm^2	2.2 m^2
Fiber I.D.(mm)	0.6	0.6
Fiber O.D. (mm)	1.0	1.0
Fiber wall thickness (μ)	200	200
Fiber length (cm)	7-14	45.5
Porosity (%)	75	75
Number of fibers	4-100	2,600
Pore size (μ)	0.1	0.1
Polymeric material	polypropylene	polypropylene

For the tests performed at Hanford with real groundwater, large size commercial ENKA modules were used.

The characteristics of the home-made laboratory scale modules used at Argonne and of the commercial modules used at Hanford are summarized in Table 3.

Permeation Experiments

All hollow-fiber modules were operated in a recirculating mode as shown schematically in Fig. 2. The feed and strip solutions were circulated through the lumen and on the shell side of the fibers, respectively, by means of calibrated peristaltic pumps. The permeation of the radionuclides through the SLM was followed by periodically sampling the feed and/or strip solution. The analyses were performed by gamma (^{59}Fe) and liquid scintillation (^{233}U, ^{45}Ca) counting techniques. The data were plotted on semilogarithmic scales as feed activity vs time. In the case of ^{233}U the data were corrected from non-uranium activity following the procedure reported in (1). From the slope of the straight line, the permeability coefficient (P) in cm s^{-1}, was calculated according to eq. 3. The membrane area was calculated as

$$A = 2\pi rNL \qquad\qquad (4)$$

where r is the internal radius of the hollow-fibers, N is the number of fibers and L their length. Some experiments were performed with large volumes of feed solution (2 liters) to demonstrate the possibility of concentrating uranium in the strip solution. The membrane module used with 2 liter feed contained 100 fibers, each 13 cm long, and was fabricated as described previously. The uranium analyses were performed by laser induced fluorescence.
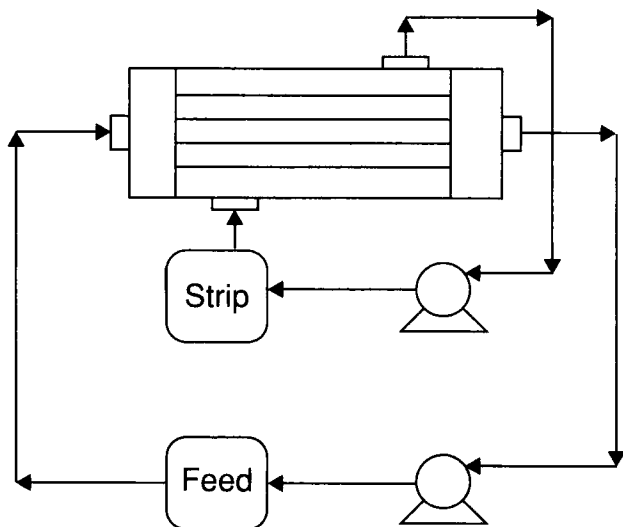

Fig. 2. Schematic description of a 4 hollow-fiber module operated in a recycling mode.

In the experiments aimed at the determination of the long-term membrane stability, a hollow-fiber module was reimpregnated several times, at time intervals of about two months, by following the procedure described in detail in ref. (6).

A module containing a carrier reservoir was also fabricated and operated according to the indications provided in refs. (6) and (7). It contained 10 fibers, each 13.4 cm long, with the top 3.2 cm in contact with about 4 cm^3 of carrier solution contained in a sealed reservoir, placed at the top of the module.

For the tests performed at Hanford using real groundwater as feed, a test stand was designed to operate two 2.2 m^2 modules in series, in parallel, or one module at a time. The test stand, shown in Fig. 3, is 150 cm high and 150 cm long, and consists of one feed tank, two strip tanks, three pumps, three rotameters, four thermocouples, and four pressure transducers. In each of the Hanford tests the volumes of the feed and strip solutions were 50 and 4 gallons, respectively.
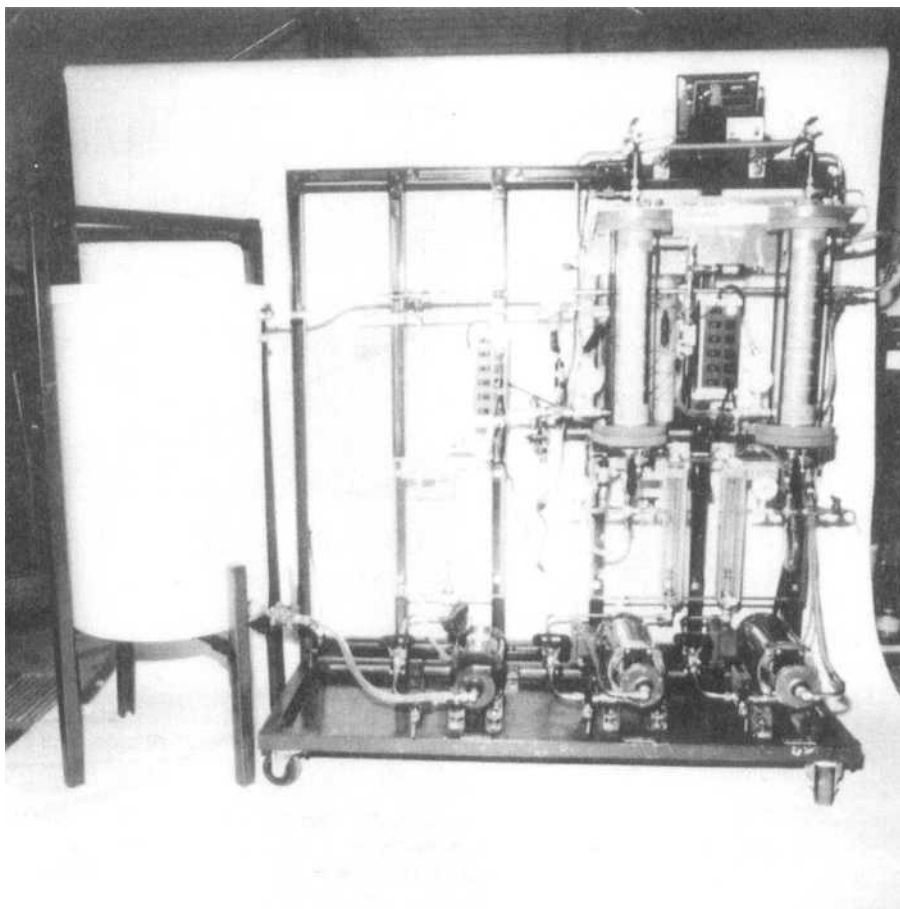

Fig. 3. Test stand used at Hanford for U(VI) removal from groundwater.

RESULTS AND DISCUSSION

1. Permeation Studies

Permeation experiments of U(VI), Ca(II), and Fe(III) have been performed with hollow-fiber supports assembled in laboratory-scale modules. The chemical conditions were the same as in the flat-sheet experiments, i.e., SGW at pH 2 was used as feed, 0.1 $\underline{M}$ HEDPA as strip, and 0.1 $\underline{M}$ Cyanex™ 272 as liquid membrane.

Fig. 4 reports a typical experiment as feed uranium activity vs time. The module used in this experiment contained 4 fibers 13 cm long, for a total membrane area of 9.8 cm^2. The feed had a volume of 13 mL and was circulated at a flow rate Q_T = 8.5 mL/min. As expected from eq. (3), the data are well aligned on a straight line up to a 99% removal of uranium from the feed.

Fig. 4. Typical uranium permeation experiment. Membrane area = 9.8 cm^2 (4 fibers, 13 cm long); feed = SGW at pH 2, 13 mL, circulated in the lumen side at 8.5 mL/min; strip = 0.1 $\underline{M}$ HEDPA, 18 mL, circulated in the shell side at 8.5 mL/min.

The optimum hydrodynamic conditions for the modules used in this work were properly identified by studying the uranium permeability as a function of the flow rate of the feed solution (lumen side). The data, reported in Fig. 5, show that a constant

P_U value was reached from a feed solution with a linear velocity equal to about 8 cm s^{-1}. At 8 cm s^{-1}, the thickness of the aqueous diffusion film (d_a) is minimized and a further increase of flow rate does not increase P_U. Furthermore, high feed velocities can be detrimental to the membrane stability. Extremely high flow rates can force the carrier solution out of the membrane pores by the excessive pressure exerted by the circulating liquid.
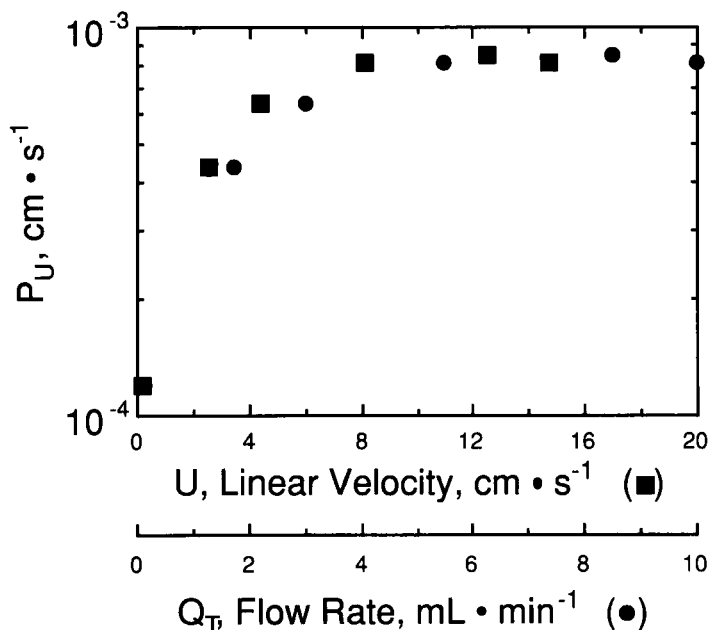

Fig. 5. P_U, U(VI) permeability coefficient vs feed flow rate, Q_T, mL min^{-1}, or feed linear velocity, $\overline{U}$, cm s^{-1}. Q_T and $\overline{U}$ are related by $Q_T = \overline{U}\pi r^2 N$, where N is the number of fibers and r their internal radius. Same conditions as in Fig. 4.

We have shown in (1) that, by plotting the uranium permeability coefficient as a function of the carrier concentration on flat-sheet supports, a "plateau" P value equal to 1.0×10^{-3} cm s^{-1} was reached for [Cyanex™ 272] $\geq 3 \times 10^{-3}$ M. In these chemical conditions the transport of U(VI) through the membrane is controlled only by the diffusion of uranium species through the aqueous phase diffusion layer at the feed-membrane interface.

From the data of Fig. 5, obtained at 0.1 M carrier concentration, one can see that, with hollow-fibers, the "plateau" value of P is 8.1×10^{-4} cm s^{-1}, which is somewhat lower than the value obtained with flat-sheet supports. Differences in P

values obtained with flat sheets and hollow fibers are attributed to the different thickness of the aqueous diffusion film because of the different hydrodynamic conditions.

Essentially the same values of the membrane selectivity coefficients for uranium(VI) over Ca(II) and Fe(III), $\alpha^M_{U/Ca}$ and $\alpha^M_{U/Fe}$, defined as the ratio of the respective permeability coefficients, were obtained using hollow-fibers or flat-sheet supports. Data in Table 4 have been calculated by using the permeability coefficient of U(VI) and the selectivity values for U(VI) over Ca(II) and Fe(III). These data show the uranium separation from SGW achievable as a function of time for a SLM process using the chemical and hydrodynamical conditions and the membrane area to feed volume ratio used in obtaining the data of Fig. 5. For a different and much higher value of the area/volume ratio, as usually provided by industrial hollow-fiber modules, the time required for a uranium separation would be correspondingly lower, but the relative contamination of uranium with calcium and iron, that depends on the selectivity, would be the same.

Table 4. U(VI), Ca(II), and Fe(III) Removal as a Function of Time from SGW at pH 2.

Conditions:
Carrier = 0.1 $\underline{M}$ Cyanex™ 272; Strip = 0.1 $\underline{M}$ HEDPA; membrane area = 9.8 cm^2; feed volume = 13 cm^3; feed linear velocity = 8.0 cm s^{-1}; P_U = 8.1 × 10^{-4} cm s^{-1} $\alpha^M_{U/Ca}$ = 1.6 × 10^4; $\alpha^M_{U/Fe}$ = 40.

Uranium removal %	Time min	Calcium removal %	Iron removal %
50.0	19	0.004	1.7
90.0	63	0.014	5.5
99.0	126	0.029	10.7
99.9	188	0.043	15.7

2. Uranium Concentration Factor

By combining the extraction and stripping U(VI)-carrier reactions taking place at the feed-membrane and at the strip-membrane interface, respectively, it is possible to show that, at equilibrium, that is when no net transport of metal takes place in either direction, and assuming the metal to be always at tracer concentration level, uranium (VI) can be concentrated in the strip solution up to about 10^8 times. Such a calculation requires the knowledge of the equilibrium constants for the U(VI)-Cyanex™ 272 reaction and for the U(VI)-HEDPA aqueous complexation reaction. The values of these constants have been reported in (1).

The very high concentration factor mentioned above is only theoretical. In practice, the uranium concentration in the feed and strip solutions is not at a tracer level and mass balance and solubility requirements will strongly reduce the achievable concentration factor.

With hollow-fiber modules operated in a recycling mode, the concentration of the transported species into the strip solution is achieved by recirculating a strip solution with a much smaller volume than the feed. Assuming a total transfer of metal, the concentration factor is simply given by the ratio of the feed to strip volumes. The same strip solution can be used over and over again until a very high metal concentration is reached. For example, we have demonstrated in (1) that a 1 $\underline{M}$ HEDPA solution, containing U(VI) at a concentration as high as 0.5 $\underline{M}$, was still effective in stripping uranium from a 0.1 Cyanex™ 272 solution in n-dodecane.

To demonstrate that high concentration factors of U(VI) can be reached in practice with our hollow-fiber modules, the experiment reported in Fig. 6 has been performed. In this experiment a module containing 100 fibers, each 13 cm long, with a total calculated membrane area of 245 cm^2, was used. The feed was a 2 liter solution of SGW circulated in the lumen of the fibers, while the strip solution volume was 45 mL (the minimum volume required to fill the shell side of the module and the tubing connections to the pump).
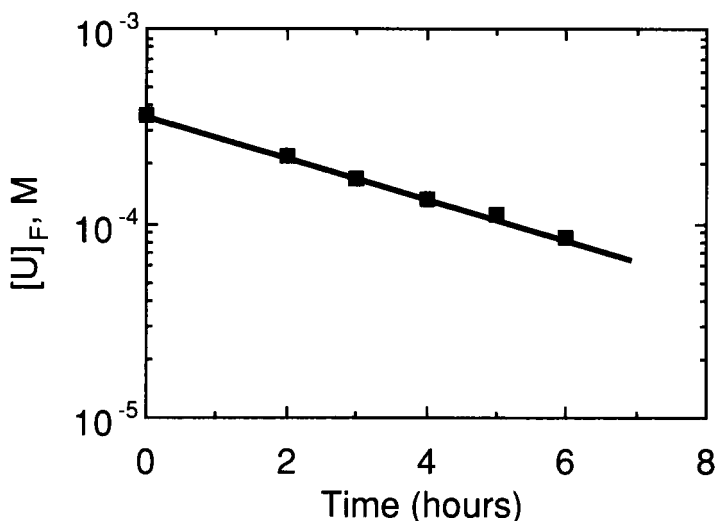

Fig. 6. Uranium(VI) permeation experiment with a high ratio of feed to strip volume. Feed = SGW at pH 2, 3.6×10^{-4} $\underline{M}$ in U(VI); strip = 0.1 $\underline{M}$ HEDPA; membrane = 0.1 $\underline{M}$ Cyanex™ 272; membrane area = 245 cm^2 calculated with eq. (4); feed volume = 2 L (lumen); strip volume = 45 mL (shell); feed linear velocity = 7.1 cm s^{-1} (Q_T = 120 mL/min); strip flow rate = 50 mL/min.

From the data of Fig. 6, a P_U = 5.8×10^{-4} cm s^{-1} was calculated. This P_U value is lower than the expected value of 8.1×10^{-4} cm s^{-1}, showing that probably the effective membrane area was lower than the calculated one. When the experiment

was interrupted after six hours, uranium had been concentrated by a factor 34 in the strip solution.

3. Membrane Stability Studies

Membrane stability experiments were performed with the objective of testing the ability of our hollow-fiber modules to continuously operate at high efficiency. The criteria for stability was a constant P_U. Two modules were used in these experiments. The first one contained 10 fibers, 10.2 cm long. The second one contained 10 fibers, 13.4 cm long, with 3.2 cm of the fiber length in contact with 4 cm^3 of the carrier solution confined in a sealed reservoir placed at the top of the module. SGW at pH 2 was continuously circulated in the lumen of the fibers, while 0.1 $\underline{M}$ HEDPA was continuously circulated in the shell side of the modules. The circulation of feed and strip solutions was interrupted only during nights and weekends. Every day the feed solution (10 mL) was replaced with fresh SGW, while the strip solution was replaced every month. Every few days the feed in both modules was spiked with ^{233}U and the transport of uranium through the SLM was followed using the usual procedure. Data have been collected over several months and are reported in Fig. 7 as P_U vs time for both the module with reservoir (MR) and the conventional module (CM).

We found that the CM module lost about 50% of its initial permeability in two months. At that point the experiment was stopped and the module was reimpregnated following the procedure reported in (6). The decline of the uranium permeability coefficient was followed again for a few months and the module was again reimpregnated. The whole procedure was repeated seven times over a total time span of almost 1.5 years. For each of the first three reimpregnations a progressively higher P value was measured with the freshly reimpregnated module, up to a P value almost twice as high as the initial one (1.5×10^{-3} cm s^{-1} vs 8.5×10^{-4} cm s^{-1}). This fact seems to confirm that some kind of interaction does take place between support and carrier solution (4), leading, in the long run, to a change in some support properties that in turn affect the permeability. A progressively more evident swelling of the fibers, for example, was observed in the CM module, with increased fiber length and membrane area. The stability of the membrane, however, did not seem to be affected by the reimpregnations, because the reimpregnated membrane did not behave differently from the original one. It is interesting that the CM module described in Fig. 7 lost about 50% of its initial uranium permeability after 6×10^5 fiber volumes had circulated through it. This value lies between the values 5×10^4 of ref. (8) and 5×10^6 of ref. (3) for similar systems, and is representative of a very stable SLM system.

In the permeation experiments performed after the last two reimpregnations, different strip solutions were used. In one case, 1 $\underline{M}$ instead of 0.1 $\underline{M}$ HEDPA was used to measure the effect of a high osmotic pressure gradient between feed and strip solutions on the stability of the membrane. The data do not show any significant decrease in stability, at least over the time interval explored, confirming that a more concentrated solution of the stripping agent can be used, which in turn means that a higher concentration factor can be reached. Similar results were obtained using 1 $\underline{M}$ VDPA as the stripping solution. The use of VDPA instead of HEDPA is recommended if a process utilizing our suggested SLM system is implemented for the decontamination of groundwater. VDPA belongs to the family of TUCS (thermally unstable complexing and stripping agents) compounds at present under investigation at ANL (5). It is almost as powerful as its parent compound, HEDPA, as a U(VI) com-

plexing agent, and is much easier to decompose by oxidation and heating, leaving the isolated uranium as a phosphate salt.
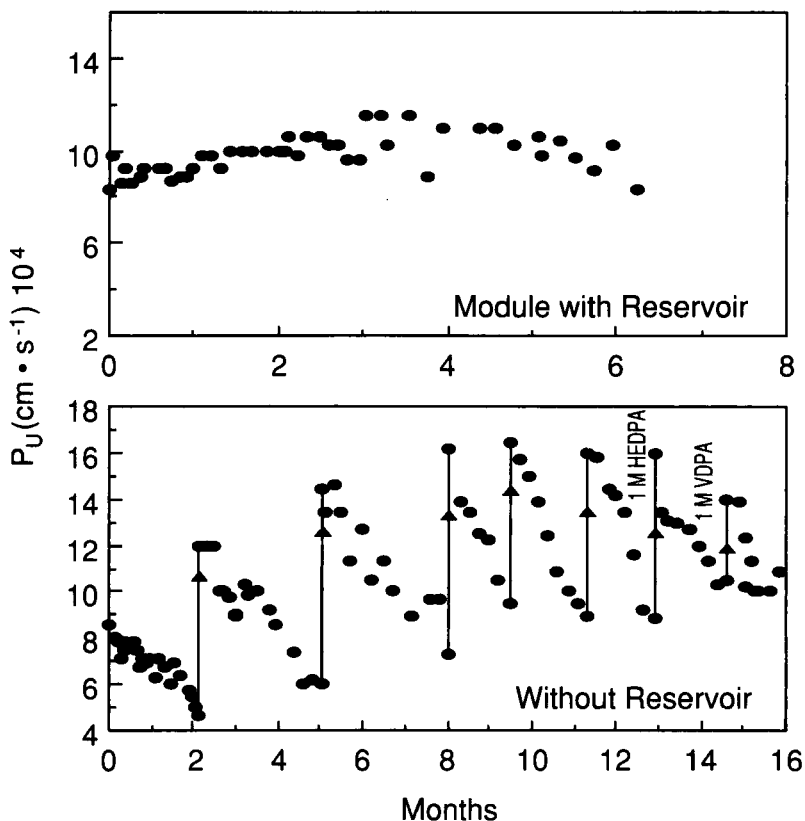
Fig. 7. P_U vs t (months) for 2 hollow-fiber modules, one without a carrier reservoir (CM), the other with a carrier reservoir (MR). Conditions: feed = SGW at pH 2, 5×10^{-4} M in U(VI), strip = see text; membrane = 0.1 M Cyanex™ 272; membrane area = 19.2 cm^2 for CM, 25.2 cm^2 for MR, calculated with eq. (4); feed volume = 10 mL, strip volume = 16 mL; feed linear velocity = 8 cm s^{-1} (Q_T = 13.6 mL/min); strip flow rate = 20 mL/min.

The MR module, equipped with a continuous reimpregnation system, performed remarkably well, which was expected from studies reported in refs. (6) and (7). We found that uranium permeability for MR actually increased by about 20% over a time span of about 110 days. The increase in P_U could be due to the same changes in membrane properties that produces a higher permeability with the CM module after

reimpregnation. Two minor problems were, however, associated with the use of a reservoir. First, it was necessary to add periodically small amounts (about 1 mL every 2-3 weeks) of carrier solution into the reservoir. It is likely that the carrier solution slowly diffuses through the fiber walls and is released to the feed and/or strip solution. This fact does not have any influence on the P_U and, actually, ensures that the support pores are always filled with relatively fresh liquid membrane solution. Second, some uranium accumulates in the reservoir solution, as revealed by analysis of periodic samples withdrawn through a suitable opening of the reservoir chamber. The uranium was extracted into the reservoir because the feed solution was circulated through the lumen side of the fibers. By circulating, instead, the feed solution on the shell side and the strip solution on the lumen side of the SLM module, reservoir contamination could probably be eliminated.

The stability experiment with the self-impregnating MR module was interrupted after about six months, because the reservoir seal deteriorated and the carrier solution leaked out. However, it worked long enough to demonstrate that a properly designed self-impregnating module can operate for a practically unlimited time.

4. Tests with Real Groundwater

Two tests were performed at Hanford using the test stand shown in Fig. 3 and groundwater from the 216-U-1,2 cribs (monitoring well 2-W19-3). The purpose of these tests was to demonstrate, using contaminated groundwater acidified to pH 2 with sulfuric acid, the SLM uranium removal process developed at Argonne on a laboratory scale. The 2.2 m^2 commercial module described in Table 3 was used after impregnation with a 0.1 $\underline{M}$ solution of Cyanex™ 272 in n-dodecane. The strip solution was 4 gallons of 0.1 $\underline{M}$ HEDPA. In each run 50 gallons of groundwater were used as feed and circulated on the shell side of the module. The results of the first run are reported in Fig. 8, as feed uranium concentration (ppb) vs time. The data show that the uranium concentration in the groundwater was reduced from 3,460 ppb to less than the Maximum Contaminant Limit (10 ppb) in less than twelve hours. Also, a straight line can be fit to the data indicating that the model described by eqs. (1-3) is valid for the module and feed conditions used in the test.

From the data of Fig. 8 a $P_U = 5.9 \times 10^{-4}$ cm s^{-1} can be calculated. The somewhat lower value than 8.1×10^{-4} cm s^{-1} reported in Fig. 5 is probably due to the poor hydrodynamics attained when the feed is circulated on the shell side of the module. The tight packing of the fibers makes it difficult to get the linear velocity required next to the fibers to minimize the aqueous diffusion layer. The second run showed, however, a better module performance, with a calculated $P_U = 1.4 \times 10^{-3}$ cm s^{-1}.

The same stripping solution was used for both runs, so that the uranium contained in 100 gallons of groundwater was collected in 4 gallons of strip solution. A much higher uranium concentration factor can be achieved, however, by using the same strip solution for other runs.

Although it is not possible to determine conclusively the scale up factor on only two runs, values obtained for the uranium permeability coefficients seem to indicate a scale up factor of one, as previously determined for the same kind of commercial modules in ref. (9).
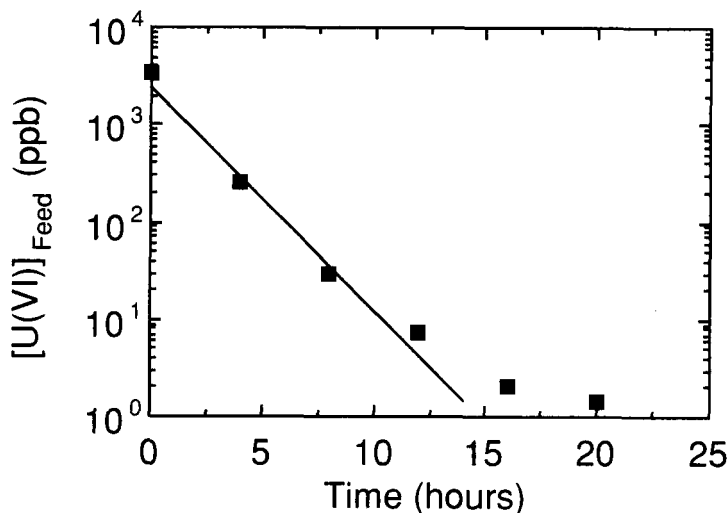
Fig. 8. Feed uranium concentration (ppb) vs time. Feed = 50 gallons groundwater (shell side); strip = 4 gallons 0.1 M HEDPA (lumen side); membrane = 0.1 M Cyanex™ 272 in n-dodecane; membrane area = 3.71 m^2 (2.2 m^2 internal area); feed flow rate = 1.5 gal/min; strip flow rate = 1.0 gal/min. Experiment performed using the test stand shown in Fig. 3.

SUMMARY AND CONCLUSIONS

We have demonstrated that a hollow-fiber supported liquid membrane system containing a carrier solution of the commercially available solvent extraction reagent Cyanex™ 272 in dodecane is very effective in removing uranium from a synthetic groundwater at pH 2. This relatively low pH value has been chosen to obtain an extremely high membrane selectivity over calcium and magnesium, which are the major constituents of the groundwater. The reagent 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) has been used as the stripping agent.

Permeation experiments, performed with small home-made hollow-fiber membrane modules have demonstrated the applicability of previously derived permeability equations to the problem of removing uranium from groundwater.

A uranium concentration factor of 34 has been demonstrated in membrane experiments. Based on the chemistry of the SLM separation investigated here, however, there is reason to believe that much higher concentration factors, of the order of at least 10^3, can be achieved without particular difficulties.

Tests performed at Hanford with real groundwater and large size commercial hollow-fiber modules have been very successful in reducing the concentration of uranium below the Maximum Contaminant Limit of 10 ppb. The uranium contained in 100 gallons of groundwater was separated and concentrated in 4 gallons of strip solution.

Very encouraging membrane stability results have been obtained with a continuously self-impregnating module with which constant uranium permeability values have been measured over a time period of more than 6 months.

It has also been shown, with a small conventional module, that the periodic reimpregnation technique is effective in restoring and actually improving the membrane performance. This experiment has been followed for one and a half years, with seven reimpregnation of the fibers, without any apparent deterioration of the membrane support. During this experiment it has been shown that a strip solution containing a 1 $\underline{M}$ concentration of the stripping agent can be used without affecting the membrane stability. Also, the use of the alternative stripping agent, vinylidene-1,1-diphosphonic acid, VDPA, belonging to the family of TUCS compounds, and more easily decomposed than HEDPA, has been tested, with positive results.

Work is in progress concerning the use of similar SLM processes for the removal of other contaminants from the groundwater.

ACKNOWLEDGMENTS

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