Use of the Donnan Equilibrium Principle to Concentrate Uranyl Ions by an Ion-Exchange Membrane Process

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Ion-exchange resins are of great utility in separation processes because they can be used to remove selectively ions from a dilute electrolyte solution. When in contact with a stripping solution of the proper composition, the resins release the ions. When the ion-exchange resins are in the form of membranes, they can be in contact with the dilute solution and the stripping solution simultaneously, and the ion-exchange process can be continuous rather than cyclic.

A continuous process with ion-exchange membranes has several advantages over an ion-exchange-resin column. Some of these are: (1) a separate regeneration step is eliminated; (2) the product has a constant composition; (3) the hold-up volume is low; and (4) operation and control of the process are simple. An advantage over a solvent extraction method is that phase-separation problems are eliminated. The membrane process is probably more economical than evaporation for concentrating extremely dilute solutions to moderate values ($\sim 0.3\ M$). In fact, ion-exchange membrane systems appear to offer unusual promise for removing small amounts of ionic materials from large-volume streams in pollution control.

The ion-exchange membrane process described here is based on the Donnan equilibrium principle and requires no electrical current or high pressure for operation, as would be required by electrodialysis or reverse osmosis. This process was first called "Donnan dialysis" by Wallace (*1*).

THEORY OF DONNAN MEMBRANE EQUILIBRIUM

Consider a system in which a porous diaphragm separates two strong electrolyte solutions. Initially the solution on the left contains only AY and that on the right, only BY_2. AY will diffuse to the right, and BY_2 will diffuse to the left until the system reaches equilibrium; then the solutions on both sides of the diaphragm will contain the same concentrations of AY and BY_2.

Next, consider the same initial conditions except this time the porous diaphragm is replaced with a cation-exchange membrane. This membrane is permeable to the cations A^+ and B^{++} but is impermeable to the anion Y and to water. A^+ and B^{++} will diffuse in opposite directions until equilibrium is reached. Donnan (2) in his original paper showed that the equilibrium concentrations of this system would be described by the generalized equation

$$\left\{ \frac{(C_i)_l}{(C_i)_r} \right\}^{1/Z} = \text{Constant}$$

for any mobile species i of valence Z. The subscripts l and r refer to the left-hand and right-hand sides of the membrane. The equilibrium concentrations for ions A^+ and B^{++} would be

$$\frac{(C_A)_l}{(C_A)_r} = \left\{ \frac{(C_B)_l}{(C_B)_r} \right\}^{1/2}$$

With the Donnan equilibrium equation and a material balance, the concentrations of AY and BY_2 on both sides of the membrane can be calculated.

The driving force that causes the B^{++} ions to move from the low-concentration phase, say, on the right to the high-concentration phase on the left is the concentration potential resulting from the difference in concentration of A^+ ions in the two solutions. The degree of separation of A^+ and B^{++} ions can be increased by one or more of the following changes in the system:

1. Increasing the initial concentration of AY in the solution on the left
2. Reducing the initial concentration of BY_2 in the solution on the right
3. Adding to the solution on the left a complexing agent that would remove B^{++} ions from that solution
4. Using a countercurrent flow system rather than the equilibrium system described above

Wallace (3) in his laboratory-scale work was able to remove more than 90% of the UO_2^{++} from a 0.01 M $UO_2(NO_3)_2$ feed solution (BY_2 in the example given) with a stripping solution of 2.0 M HNO_3 (AY) in a countercurrent-flow system. The concentration of UO_2^{++} in the product was 25 to 30 times greater than in the feed.

DESIGN CRITERIA

The design goal was to produce a flat-membrane device to concentrate a feed of 0.01 M uranyl nitrate to about 0.25 M by a continuous process. Because addition of different ionic species was undesirable, nitric acid was used as the stripping solution to supply hydrogen ions to cause the transfer of uranyl ions from the feed to the stripping stream.

MEMBRANES

In recent years a variety of both anion- and cation-exchange membranes have become commercially available. For testing and design of the membrane systems described here, AMFion C-103 membranes* were used. These were flat sheets of polyethylene-styrene graft copolymer with fixed-charge anions, formed by treating the graft copolymer with chlorosulfonic acid. The fixed-charge concentration is about 1.3 meq./g. of dry weight.

Although cation-exchange membranes tend to exclude anions, the exclusion is not complete. Leakage of nitrate ions would cause a transfer of hydrogen ions without the corresponding transfer of uranyl ions, thus causing a loss

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of hydrogen ions to the transfer process. Hence, an excess of acid would be required. Since two hydrogen ions must be transferred for each uranyl ion, this is the theoretical minimum ratio of hydrogen ion to uranyl ions required for complete transfer. Wallace (*1*) defined a ratio α to express this relationship as follows:

$$\alpha = \frac{\text{equivalents of anions in the stripping stream}}{\text{equivalents of cations in the feed stream}}$$

Thus, $\alpha = 1$ when the ratio of hydrogen ions to uranyl ions is 2 because uranyl ions are divalent.

With the AMFion C-103 membrane, Wallace found the optimum value of α to be about 1.5 for the nitric acid-uranyl nitrate system.

EXPERIMENTAL AND RESULTS

To determine overall mass transfer rates through a membrane with various flow conditions about it, an apparatus was constructed in which an AMFion C-103 membrane separated two circulating streams and in which the flow rates of the two streams could be varied independently over a wide range. The apparatus was charged with nitric acid-uranyl nitrate solutions with concentrations of interest, but different for each side of the membrane, and these solutions were circulated until equilibrium was reached as shown by chemical analysis.

The results from the above experiments indicated that the overall transfer rate for uranyl ions was strongly dependent on both the flow rate and the concentration of uranyl ions on the dilute side. Thus, the rate-limiting step was the diffusion of uranyl ions from the dilute solution to the membrane.

Calculations by Wallace (*4*) indicated that, with flow channels 15 mils thick or less, the major resistance to mass transfer would be in the membrane. Experiments with both 30- and 15-mil-thick channels have shown higher overall transfer rates than with thicker channels, thereby requiring less membrane surface. On the basis of this information, it was decided that the solution channels should be made as thin as fabrication techniques would allow.

The means of the entry and exit of countercurrent-flowing solutions in a thin-channel membrane concentrator are shown in Figure 1. The stainless steel (304) screens are spot-welded to stainless shim stock. The screens support the membrane and maintain the uniformity of channel thickness. The spacers around the edges of the screens are made of polyethylene and have cut into them the entry and exit ports. Five membranes are connected in series and then groups of five are connected in parallel. The entire device is about 20 in. long, 6 in. wide, and several inches thick depending on the membrane area required. Pressure drops are less than 5 psi.

Osmosis is one of the big problems involved in this device because of the dilution effect resulting from the transport of water into the stripping stream. It was found that recycle of a portion of the stripping-stream effluent (extract) to the inlet decreased the dilution of the extract by osmosis. Without recycle, there are no uranyl ions in the entering stripping stream, and the membrane is evidently in the hydrogen form in that region. With recycle, more of the membrane is in the uranyl form, in which form it apparently is less permeable to water than in the hydrogen form.

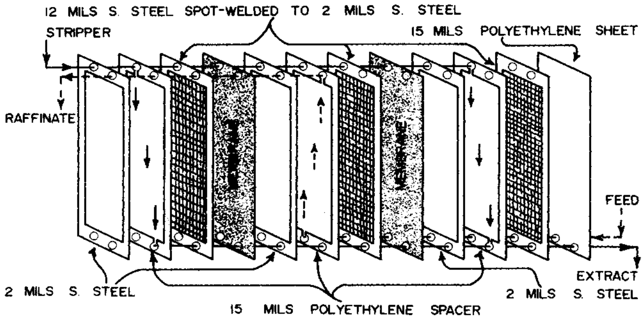

Fig. 1. Exploded view of membrane concentrator.

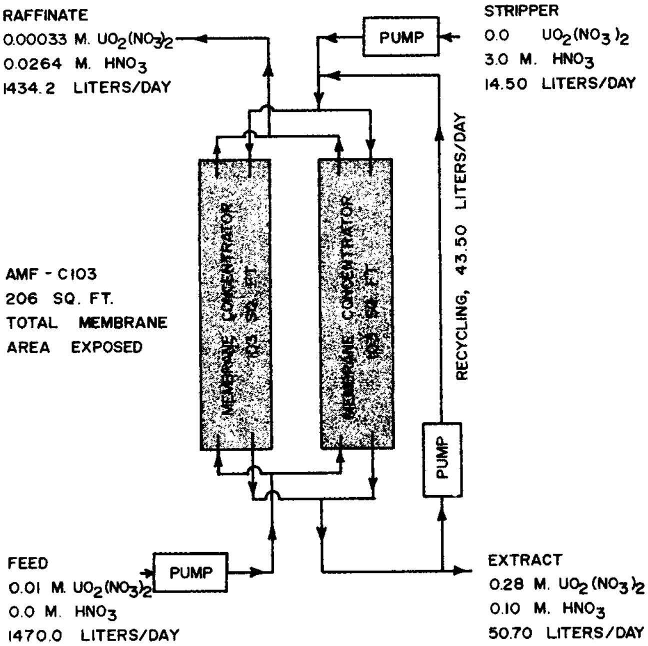

Fig. 2. Proposed thin channel concentrator.

Experimental data in the table show the effects of recycle. With increasing recycle ratio θ, the recovery of uranyl ions increased (lower uranyl-ion concentrations in the raffinate), the product was more concentrated (higher uranyl-ion concentration in the extract), and the osmotic transport of water was reduced. It should also be noted that, when the stripping stream was 3 M HNO_3, the uranyl-ion recovery and the product concentration were higher, but the 2 M HNO_3 stripping solution caused less dilution of the product by osmosis.

FINAL DESIGN

The final design of the system to concentrate uranyl nitrate is shown in schematic form in Figure 2. With 206 sq. ft. of membrane area, it has the capacity to concentrate 3.5 kg. of uranium per 24 hr. to 0.25 M from a feed of 0.01 M uranyl nitrate. The recovery of uranium is 96% or better. Osmosis is reduced by recirculating a portion of the extract stream to keep the membrane in the uranyl form. Solution channels are 15 mils thick.

Because of anion leakage, the extract (product) uranyl nitrate solutions contain small amounts of nitric acid. Wallace (*1*) has shown excess acid can be removed by Donnan dialysis with anion-exchange membranes and sodium hydroxide stripping solution.

CONCLUSIONS

Donnan dialysis appears to be an attractive method for recovering ions from dilute solutions. Because it is a continuous process, it might be expected to replace cyclic processes that employ ion-exchange beads. Overall mass transfer rates in a membrane concentrator can be increased by utilizing thin solution channels, and dilution of the product by osmosis can be reduced by recycling a portion of the product to the stripping stream. It is believed that the removal of pollution consisting of ionic species by this method holds unusual potential.

TABLE 1. MULTIPLE-PASS MEMBRANE CONCENTRATOR
(Feed concentration, $UO_2^{++} = 0.01$ molar)

RUNS	Flow Rate Ml./hr. Feed	Flow Rate Ml./hr. Strip.	UO_2^{++} Conc. Molar Raf. $\times 10^3$	UO_2^{++} Conc. Molar Ext.	H^+ Conc. Molar Raf. $\times 10^2$	H^+ Conc. Molar Ext.	$\frac{\text{EXT.}}{\text{STR.}}$	α	θ	UO_2^{++} Flux $\times 10^5$ $\frac{\text{Moles}}{\text{sq. in., hr.}}$	Osmosis $\times 10^3$ $\frac{\text{Moles}}{\text{sq. in., hr.}}$
Stripping concentration, $H^+ = 2.0$ molar											
4	3810	72.5	0.78	0.204	2.78	0.145	2.50	1.90	0.0	1.68	2.74
13	1654	22.8	0.75	0.262	2.56	0.071	2.48	1.38	1.0	1.85	2.34
14	1699	25.1	0.45	0.292	2.61	0.104	2.26	1.48	2.0	2.07	2.19
17	1646	24.7	0.38	0.300	2.60	0.135	2.25	1.50	3.0	2.09	2.15
Stripping concentration, $H^+ = 3.0$ molar											
29	1698	18.4	0.437	0.2440	2.55	0.121	3.64	1.62	0.0	2.04	3.37
25	1678	15.8	0.455	0.3093	2.71	0.057	3.31	1.41	1.0	2.02	2.54
24	1669	16.3	0.397	0.3168	2.71	0.088	3.18	1.47	2.0	2.05	2.47
35	1681	16.1	0.387	0.3180	2.69	0.096	3.14	1.44	3.0	2.01	2.40

$\frac{\text{EXT.}}{\text{STR.}}$ = volumetric ratio of extract to strip streams

ACKNOWLEDGMENT

The authors are indebted and grateful to the Savannah River Office of the Atomic Energy Commission for support of this work under Contract AT (38-1)-525.

NOTATION

a = activity
C = concentration
E_{Don} = Donnan potential
F = Faraday's constant
M = molar
R = gas constant
T = absolute temperature
Z = valence
α = ratio of equivalents of ions in strip stream to equivalents of ions in feed stream
valents of ions in feed stream
θ = recycle ratio; ratio of volumetric flow rate of recycling extract to volumetric flow rate of make-up stripping acid.

Subscripts

l = left side
r = right side

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Separation of Shape and Polarity Effects for Polar Fluids

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In recent papers, Halm and Stiel have defined a fourth parameter for polar fluids through the vapor pressure and have shown that this approach is applicable for the entropy of vaporization (*1*), density of saturated liquids and vapors (*2*), and second virial coefficients (*3*). This method has been successfully applied also for other properties, including the heat capacity of saturated liquids (*4*), and surface tension of polar fluids (*5*). In the definitions of the shape and polarity parameters ω and x, the effects of the different types of molecular interaction are not separated, so that although the parameters have considerable utility, they do not each have direct physical significance.

The reduced vapor pressure of a polar fluid can be expressed as

$$P_R = f\left(T_R, \frac{a}{\rho_0}, \frac{\mu^2}{\epsilon \rho_0^3}\right) \tag{1}$$

where a/ρ_0 is the shape group and $\mu^2/\epsilon\rho_0^3$ the polarity