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Reverse Osmosis Performance of Cellulose Acetate Membranes in the Separation of Uranium from Dilute Solutions

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Abstract

Batch 316–type cellulose acetate membranes were characterized in terms of pure water permeability constant, solute transport parameter, and mass transfer coefficient with a reference system of aqueous sodium chloride solution. These membranes were used in the determination of reverse osmosis characteristics such as product rate and solute separation in the case of uranium sulfate solutions of different concentrations (100 to 8000 ppm) in the feed solutions. A long-term test extending over a week has been carried out with dilute uranium solutions. Reverse osmosis treatment of synthetic mine water sample showed satisfactory performance of the membranes in the separation of metal ions.

INTRODUCTION

Recently a review on "Reverse Osmosis for the Treatment of Metal Waste Solutions" covering factors such as principles, physicochemical criteria for the separation of metal ions, factors which influence the stability of membranes, and the application of the process for the treatment of electroplating waste solutions and acid mine drainage water has

been published (*1*). Studies on the performance of cellulose acetate membranes in the reverse osmosis behavior of metal ions such as Cu^{2+}, Ni^{2+}, Fe^{3+}, and Al^{3+} have been carried out, and the results have been applied with success in the treatment of a sample of acid mine water (*2*).

There exist many possible sources of pollution in the mining and processing of uranium from ores. These include pit water from mining operations, contaminated water from weathering of overburden, below-ore-grade material and ore stockpiles, solid tailings remaining after leaching of ore, and liquid effluents arising from purification and subsequent chemical operations. The liquid effluents from treatment plants, in particular the raffinate or barren liquor discharged after the recovery and purification of the uranium from the leach liquors, have to be subjected to a process by which water free of toxic metal contaminants is produced before discharge to rivers or streams. The composition of barren liquors depends on the type of process used, such as acid or alkaline leaching followed by ion exchange, or a solvent extraction method of purification. In either case the barren solution contains traces of heavy metal impurities, and these solutions should be treated both from the points of view of water pollution control and waste recovery.

In general, effluent solutions may be disposed of, with or without suitable treatment, by discharge into rivers and streams after dilution, evaporation from tailings dams or ponds, or deep well injection depending on environmental considerations. The extent to which the waste effluents have to be free of contaminants is dependent on the method of storage or discharge in the environment. Even though methods for the complete retention of effluents in tailings and dams are cited in the literature (*3*), alternate methods of treatment for the removal of pollutants to environmentally acceptable levels may be necessary in view of the possibility of release of pollutants due to seepage to ground waters, accidental overflow, and/or structural failure.

One of the most promising methods for desalinization and concentration of aqueous salt solutions and their purification is reverse osmosis, which does not involve phase transformation of the liquid. Decreased expenditure of energy, simplicity of the processing technology, and the operation of the process at normal ambient temperatures are some of the attractive features of the reverse osmosis process. The high capital investment and the membrane compaction problems make the reverse osmosis process at high pressures prohibitive. Thus the reverse osmosis treatment of metallurgical waste effluents at low pressures ($\sim$300 psi) is attractive and can result in both reduction of water pollution and production of

product water which can be used in recycling operations. Cellulose acetate membranes with significantly high productivities at low operating pressures (~300 psig) have been developed recently (*4*). These membranes were obtained by a judicious optimization of variables such as the composition and temperature of the casting solution and the solvent evaporation rate during the formation of the film. The membranes designated as Batch–316 are the most promising for low-pressure reverse osmosis application. The detailed studies reported in this paper are concerned with the performance of Batch-316 cellulose acetate membranes in the reverse osmosis treatment of uranium solutions under a variety of conditions.

EXPERIMENTAL

Nonflow Type Apparatus

The static cell and the schematic diagram of the nonflow-type experimental set-up are illustrated in Figs. 1 and 2. The static cell (Fig. 1) was made of stainless steel and consisted of two detachable parts. The membrane rested on a stainless steel porous plate embedded in the lower part of the cell. The product solution permeating through the membrane was withdrawn at atmospheric pressure from an outlet provided in the lower part of the cell. The top part of the cell contained the feed solution under pressure in contact with the membrane. The two parts of the cell were fitted and sealed by the use of rubber O-rings. The effective area of the membrane surface in the cell was 9.6 cm^2. Pressurization was afforded by compressed nitrogen gas from a gas cylinder. During the experiment the feed solution was stirred by a magnetic stirrer fitted in the cell about 0.25 in. above the membrane.

Flow-Type Apparatus

The dynamic or continuous flow-type cell and the flow diagram of the apparatus used are illustrated in Figs. 3 and 4. The cell, fabricated from 310 stainless steel, consisted of two detachable parts. The upper part was provided with inlet and outlet openings for the flow of the feed solution under pressure. The bottom part, provided with an outlet for the withdrawal of the membrane-permeated product solution, was the support for the membrane. The preshrunk cellulose acetate membrane was mounted on a stainless steel porous plate embedded in the bottom part

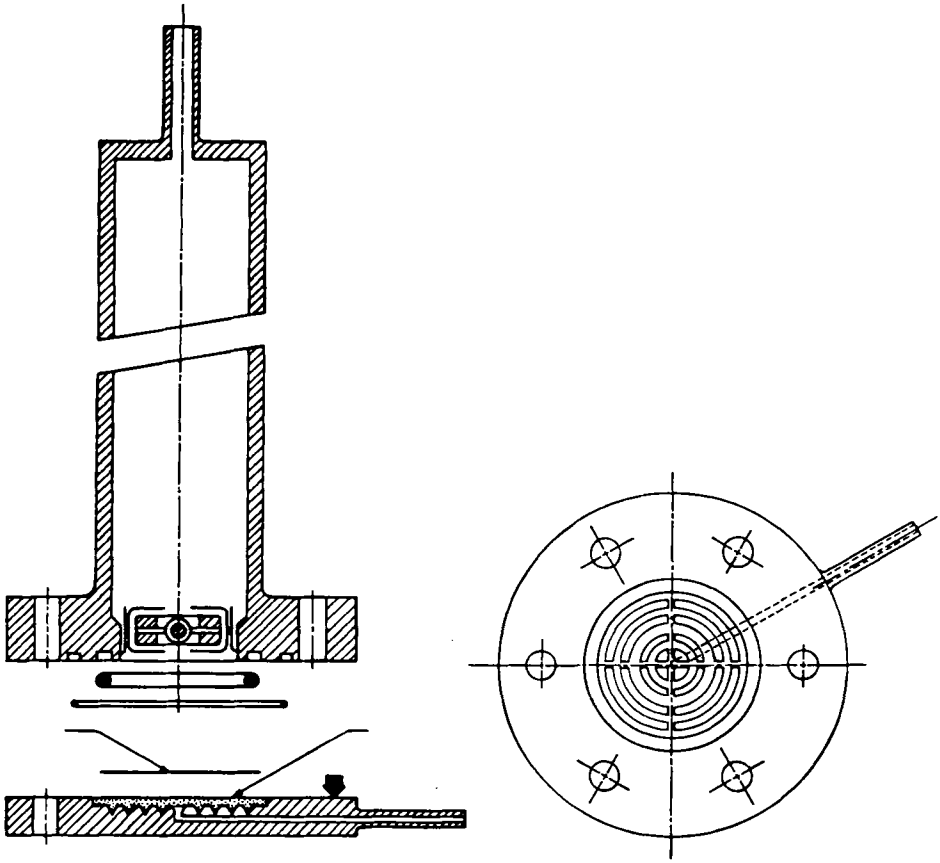

FIG. 1. Static cell.

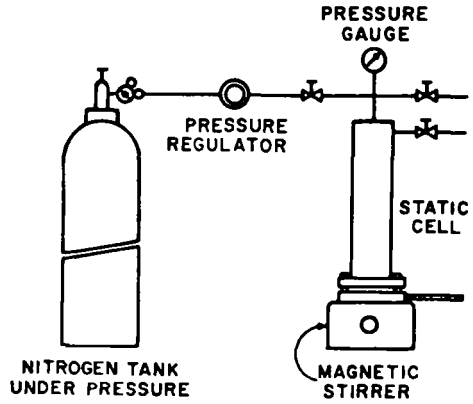

FIG. 2. Schematic diagram of nonflow type apparatus.

of the cell, and the effective surface area of the membrane was 7.6 cm^2. The top and the bottom parts of the cell were fitted to proper alignment with rubber O-rings between the high-pressure chamber and the membrane. Clamping the cell between two thick end-plates provided a pressure-tight joint. As depicted in the schematic diagram (Fig. 4), a high-pressure pump (BIF) was used. All parts of the pump coming into contact with the feed solution were made of either Hastalloy or stainless steel. A hydraulic accumulator was used as the surge tank to minimize pressure fluctuations in the cell. During an experiment the fluid pressure in the cell was indicated by a calibrated glycerine-sealed pressure gauge. Constant

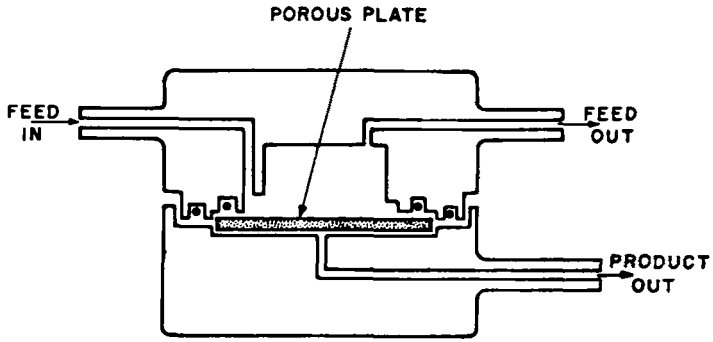

FIG. 3. Flow-type cell.

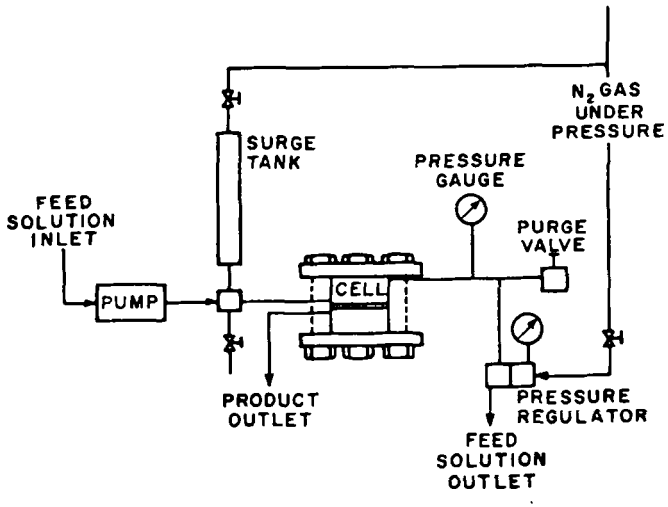

FIG. 4. Schematic diagram of flow-type apparatus.

operating pressure in the cell was maintained by a stainless steel pressure gauge. Whenever necessary, the system was drained by a purge valve. The dome of the Grove pressure regulator was filled with nitrogen gas under pressure. Monel high-pressure tubing, and fittings made of 316 stainless steel, were used throughout the system, which was designed for operation at pressures much higher than those used in the present studies. Six cells were used in series so that six different membranes could be tested simultaneously for their performance. The pressure drop in the system was low and of the order of 10 psig.

PROCEDURE

All the experiments were carried out at the laboratory temperature (23 to 25°C). The membranes, after being subjected to shrinkage at various temperatures under water, were then pressurized with pure water at 300 psig for about 2 hr before subsequent use in reverse osmosis experiments at an operating pressure of 250 psig. In every experiment the pure water permeation rate, the membrane permeated product rate per given area of membrane surface, and the solute separation (f) were determined at preset operating conditions. Aqueous feed solutions containing sodium chloride at a concentration of 3500 mg/l were used to

obtain data on membrane specifications and to specify the mass transfer coefficient on the high-pressure side of the membrane. The product rate data reported are accurate to within 3%. As reported before (*2*), low metal ion concentrations are involved, and hence the solute separation data were calculated by the relation:

$$f = \frac{\text{solute conc in feed} - \text{solute conc in product}}{\text{solute conc in feed}}$$

The concentrations of sodium chloride in the feed and the product solutions were determined by specific resistance measurements. Uranium solutions were analyzed by a spectrophotometric method (*5*) using 1-(2-pyridylazo)-2-naphthol (PAN). This method consisted of mixing the uranium solution with 5 ml of ammonia–ammonium chloride buffer solution followed by 2 ml of 0.1 *M* EDTA solution, 2.0 g of sodium chloride, and 2 ml of PAN. After 5 min the uranium complex of PAN was extracted into 10 ml of chloroform and the absorbance measured at 560 nm against a reagent blank. The concentrations of other metal ions used in this study were determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Film Casting, Membrane Specifications, and Feed Flow Conditions

The composition of the film-casting solution and specification of the film-casting conditions for the Batch-316 cellulose acetate membranes used in the present study are given in Table 1. The emergence of this type of membrane is the result of a new approach to the general problem of developing more productive cellulose acetate membranes. In this approach the structure of the casting solution and the rate of evaporation of the solvent during the formation of the film constitute the important interconnected variables governing the ultimate porous structure, and hence the performance, of the resulting membranes in reverse osmosis processes.

Reverse osmosis membranes can be specified in terms of the pure water permeability constant, A, and the solute transport parameter, D_{AM}/K_δ, at a particular operating pressure. The flux and solute separation obtainable with a membrane so specified is a function of the mass transfer coefficient, k, on the high-pressure side of the membrane, which is determined by the feed flow rate and the feed concentration used in the

TABLE 1

Film-Casting Conditions

Parameter	Value
Film type	CA-NRC-316 (Batch-316)
Composition of casting solution, wt-%:	
Cellulose acetate (Eastman 398–3)	17.00
Acetone	69.20
Magnesium perchlorate	1.45
Water	12.35
Temperature of casting solution, °C	0
Temperature of casting atmosphere, °C	24
Casting atmosphere	Ambient air in contact with aqueous solution of 30 wt-% acetone
Solvent evaporation time (min)	6
Duration of film-setting in ice-cold water (hr)	>1
Nominal film thickness (cm)	0.01

TABLE 2

Film Specifications Data

Film no.	1	2	3	4	5	6
Pressure, 250 psig						
Film shrinkage temperature (°C)	82	80	78.5	76	72	75.5
Pure water permeability constant $A\left(\frac{\text{g mole } H_2O}{\text{cm}^2 \text{ sec atm}} \times 10^6\right)$	1.78	2.47	3.00	4.10	5.39	3.84
Solute transport parameter $(D_{AM}/K_\delta)_{NaCl}$ [(cm/sec) × 10^5]	4.55	9.63	17.59	35.28	99.2	44.17
Solute separation (%)	90.6	85.6	78.9	72.7	52.6	64.3
Product rate (g/hr)[a]	21.89	30.40	37.11	51.62	69.64	48.43

[a]Area of film surface, 13.2 cm^2. Film pressurized at 300 psig. Feed concentration, 3500 ppm NaCl–H_2O. Mass transfer coefficient, 56.34 × 10^{-4}.

experiment. A computer program (*6*) involving experimental data on pure water permeation rate, membrane permeated product rate, and solute separation at preset operating conditions for the aqueous sodium chloride feed solution containing 3500 mg/l salt was used in the calculation of A, D_{AM}/K_δ, and mass transfer coefficient, k. The data given in Table 2 on the values of A and D_{AM}/K_δ for sodium chloride at 250 psig specify the membranes used in the present studies. The feed flow conditions used

in all the experiments carried out in the present study are specified in terms of the corresponding values of k obtained with the reference sodium chloride solution system containing 3500 mg/l salt. In order to compare relative performance of different membranes for feed solution systems for which physicochemical data such as osmotic pressure and other relevant data are not readily available, it is useful to provide such specifications for membranes and the feed flow conditions used in terms of easily obtainable parameters for a convenient and well-studied reference feed solution system such as sodium chloride solution. The data given in Table 2 show the high productivity of Batch-316 cellulose acetate membranes at low operating pressures.

Data on Solute Transport Parameter

The experimental data on solute separation (f) and product rate (PR) were used in the calculation of solute transport parameter for the solute of interest, using different membranes, from the equation

$$D_{Am}/K_\delta = \frac{PR}{3600sd}\frac{1-f}{f}\left(\exp\frac{PR}{3600kd}\right)^{-1}$$

where s is the effective membrane surface area (13.2 cm^2), d is the density of the solution, and k is the mass transfer coefficient on the high-pressure side of the membrane. The values of mass transfer coefficient, k, were obtained employing the equation

$$k = k_{ref}\left[\frac{(D_{AB})}{(D_{AB})_{ref}}\right]^{2/3}$$

where k_{ref} is the mass transfer coefficient for the reference system of 3500 ppm of aqueous sodium chloride (56.34×10^{-4} cm/sec), and $(D_{AB})_{ref}$ and D_{AB} refer to the diffusivity of sodium chloride and the salt in question, respectively.

The diffusivity values (D_{AB}) in cm^2/sec of the solutes used in the present investigation were obtained from the Nernst equation

$$D_{AB} = \frac{\left(\frac{1}{Z_+} + \frac{1}{Z_-}\right)RT}{\left(\frac{1}{\lambda_+} + \frac{1}{\lambda_-}\right)F^2}$$

In the above equation, Z_+ and Z_- are the valencies of the cation and anion, respectively, R is the gas constant (8.314 J °K^{-1} mole^{-1}), T is

TABLE 3
Data on Solute Transport Parameters

Salt	Solute separation	Product rate	k (cm/sec)	D_{AM}/K_δ (cm/sec)
UO_2SO_4	0.9953	34.64	29.50×10^{-4}	3.441×10^{-6}
	0.9937	42.11		5.616×10^{-6}
	0.9833	60.51		2.161×10^{-5}
	0.9660	81.81		6.055×10^{-5}
	0.9860	56.77		1.695×10^{-5}
	0.9948	24.78		2.725×10^{-6}
	0.9949	34.24		3.692×10^{-6}
	0.9945	41.62		4.842×10^{-6}
	0.9846	59.78		1.967×10^{-5}
	0.9620	81.00		6.728×10^{-5}
	0.9820	56.13		2.164×10^{-5}

the absolute temperature, λ_+ and λ_- are the limiting ionic conductance values (ohm^{-1} cm^2 equiv^{-1}), and F is the Faraday. The values of solute transport parameter, D_{AM}/K_δ, along with solute separation and product rates are presented in Table 3. As expected, the value of solute transport parameter increases with a decrease in solute separation and with an increase in product rates.

Separation of Uranyl Sulfate Solutions

The effect of varying the concentration of uranyl sulfate on the reverse osmosis characteristics such as product rate (flux rate) and percent solute separation was studied. Experimental data on the flux rate and percent solute separation for the feed concentration range of 100 to 8000 ppm of uranyl sulfate are presented in Table 4. These data were obtained using flow-type cells with which high mass transfer coefficients were obtained on the high-pressure side of the membrane. Because bivalent salts, such as uranyl sulfate, are better separated than monovalent salts, such as sodium chloride, the average pore size on the membrane surface needed to yield a given level of solute separation is higher for uranyl salts than that needed for sodium chloride. The effect of the variation of the concentration of uranyl sulfate in the feed solution on the flux rate is shown in Fig. 5. It is clear from this figure that the drop in flux rate is insignificant in the range of 10.7 to 26.0 gal ft^{-2} day^{-1} up to a feed concentration of 8000 ppm of uranyl sulfate. The percent solute separation obtained as a function of the feed concentration is depicted in Fig. 6. Reference to Table 4 and Fig. 6 shows that solute separation of more than 99% is obtained up to a concentration of 8000 ppm of uranyl sulfate. The flux rate cor-

TABLE 4

Data on Solute Separations[a]

Salt (ppm)	Film 1		Film 2		Film 3		Film 4		Film 5		Film 6	
	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate
UO_2SO_4 (100)	98.42	10.74	99.32	14.83	99.23	18.02	98.26	26.08	96.95	35.40	95.68	24.49
UO_2SO_4 (100)	—	10.23	—	14.49	—	17.62	97.18	25.55	90.91	34.82	95.55	24.02
UO_2SO_4 (500)	—	11.17	99.53	15.45	99.37	18.79	98.33	27.01	96.60	36.51	98.60	25.33
UO_2SO_4 (500)	99.48	11.06	99.49	15.28	99.45	18.57	98.46	26.68	96.20	36.14	98.20	25.04
UO_2SO_4 (1000)	99.48	11.04	99.57	15.26	99.50	18.55	99.00	26.69	94.70	36.17	97.00	25.07
UO_2SO_4 (1000)	—	10.74	99.64	14.86	99.60	18.08	98.84	26.06	96.40	35.48	98.40	24.55
UO_2SO_4 (4000)	—	10.96	99.77	15.10	99.74	18.31	97.73	26.39	94.03	35.67	95.95	24.73
UO_2SO_4 (4000)	99.45	10.36	99.75	14.27	99.73	17.30	97.90	24.92	96.45	33.65	96.29	23.37
UO_2SO_4 (8000)	99.46	10.75	99.71	14.77	99.36	17.86	97.61	25.75	94.95	34.26	96.39	23.97
UO_2SO_4 (8000)	99.44	10.13	99.69	13.93	99.34	16.87	97.59	24.31	94.93	32.30	96.38	22.62

[a]Product rate in gal day^{-1} ft^{-2}.

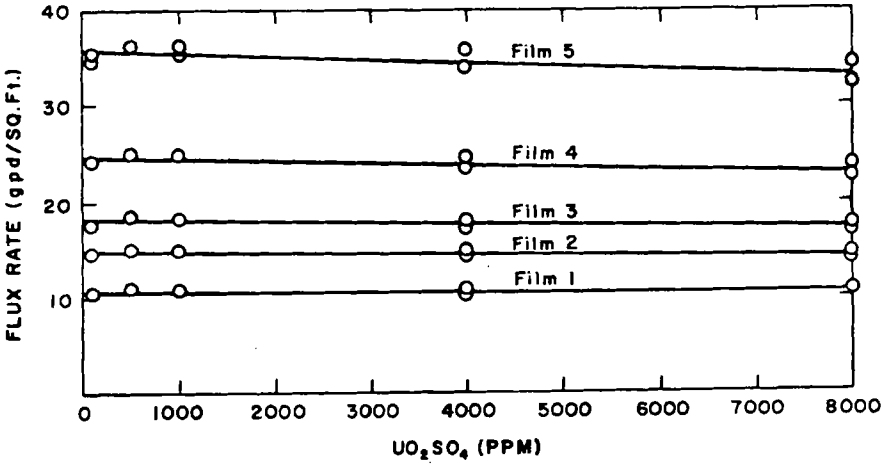

FIG. 5. Effect of uranium feed concentration on flux rate.

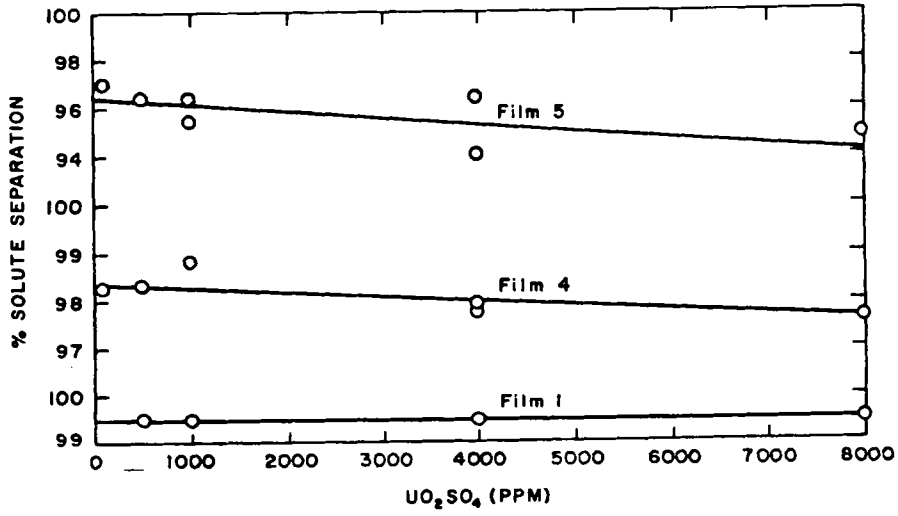

FIG. 6. Effect of uranyl ion concentration on solute separation.

TABLE 5

Solute Separations and Flux Rate[a]

Days	Film 1		Film 2		Film 3		Film 4		Film 5		Film 6	
	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate
0	96.55	11.31	96.60	15.67	93.20	18.96	93.60	25.98	83.80	33.92	86.75	24.26
1	98.02	10.64	96.37	14.73	95.19	17.83	97.03	24.46	91.69	32.01	93.27	22.72
2	99.69	10.52	98.64	14.56	98.19	17.50	98.28	24.19	95.84	31.20	96.41	22.24
3	99.27	10.16	99.28	11.63	99.04	10.81	98.82	13.95	97.58	11.62	95.27	9.80
4	99.19	7.87	99.05	5.19	98.66	6.15	—	8.24	94.91	7.32	96.86	6.10
7	99.37	4.52	99.00	3.87	98.95	3.83	97.75	5.35	93.31	5.04	95.18	4.12

[a]Feed concentration = 1000 ppm UO_2SO_4. Operating pressure = 250 psig. Product rate = gal day^{-1} ft^{-2}.

responding to this degree of solute separation is 18.0 gal ft^{-2} day^{-1}. The high level of solute separation (>99%) obtained with the first three membranes (Table 5) shows that the membrane pore sizes represented by (D_{AM}/K_δ) for sodium chloride values up to 17.59×10^{-5} cm/sec are suitable for use in the treatment of dilute uranium solutions under the experimental conditions used in the present work. The product rates obtained with film 5 are the highest, and progressively less with membranes shrunk at higher temperatures. From this discussion it can be concluded that membranes 1, 2, and 3 (Table 4) are adequate for the separation of uranyl sulfate, but film 3 is the best from the point of view of maximum product rate and high degree of separation.

The results discussed so far refer to short period runs extending over 2 hr. Under conditions of continuous operation for longer periods of time, the membranes tend to compact, resulting in lower product rates. The latter yields are of practical interest from the point of view of process

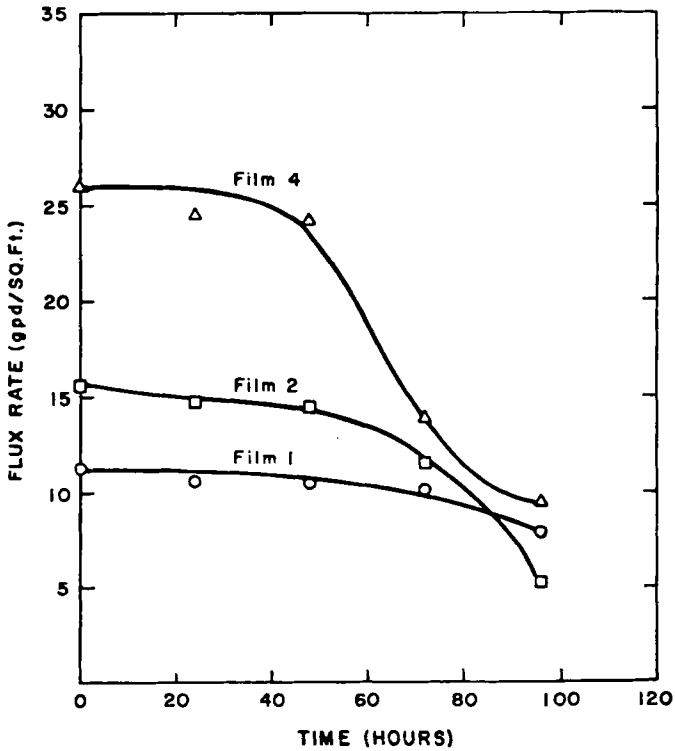

FIG. 7. Flux rate as a function of time.

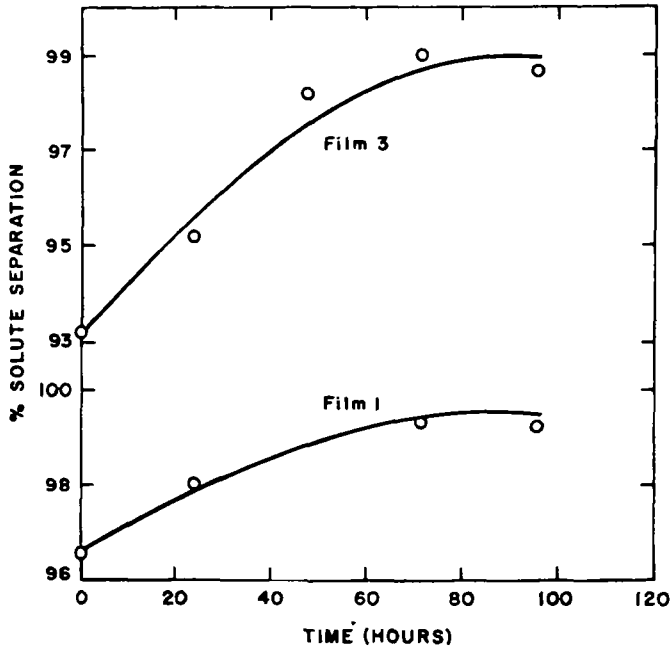

FIG. 8. Solute separation as a function of time.

design. Hence a week-long continuous test run was carried out to assess the performance of the membranes, using dilute uranyl sulfate solution as the feed. The operating pressure was 250 psig, the concentration of uranium was 1000 ppm, and the feed flow conditions were similar to those used in short-run tests. The solute separation and the product rates were determined at regular intervals during the test period. The results obtained from long-term runs are presented in Table 5 and illustrated in Figs. 7 and 8. There is a small decrease in the flux rates up to 48 hr followed by a more pronounced decrease in the case of all the membranes except the first. The initial small decrease in flux rate may be attributed to the effect of membrane compaction on the permeation rate. The progressive decrease in flux rate (after 48 hr) can be attributed to clogging of the membrane pores by uranium oxide particles produced as a result of hydrolysis of the uranyl ion. The progressive increase in solute separation (Fig. 8) can also be attributed to the clogging of pores by uranium oxide particles. After the test period the membranes were washed with dilute perchloric acid (0.01 *M*) and restored to their original condition as evidenced by the

TABLE 6
Data on Separation of Metal Ions in Mine Water (ppm)

	Ca^{2+}	Fe^{3+}	Al^{3+}	U^{6+}	Product rate[a]
Mine water feed	52	30	10	30	—
Product water Film 1	0.6	<0.1	<1	<0.5	11.1
Product water Film 2	1.3	0.4	<1	<0.5	15.4
Product water Film 3	2.0	0.4	<1	<0.5	18.7
Product water Film 4	2.7	0.6	<1	0.5	26.9
Product water Film 5	7.0	2.0	<1	1.1	36.3
Product water Film 6	4.8	1.8	<1	0.5	25.2

[a]Gal day^{-1} ft^{-2}.

solute separation and product rates obtained with 3500 ppm of sodium chloride solution.

A synthetic sample of acid mine water containing iron, calcium, aluminum, and uranium was subjected to reverse osmosis treatment, and the results obtained are presented in Table 6. From the results it can be concluded that film 1 gave the best separation of metal ions with a product rate of 11.1 gal ft^{-2} day^{-1}. A comparison of the data given in Table 6 with those in Table 2 shows that the separation of metal ions is in keeping with the membrane specifications and performance data.

CONCLUSIONS

Reverse osmosis treatment of dilute uranium solutions with cellulose acetate membranes has been carried out and the reverse osmosis characteristics determined. This method has been applied to the treatment of acid mine water (synthetic sample) and found to contribute significantly to both water pollution control and the recovery of metals and pure product water. With Batch 316-type cellulose acetate membranes, the treatment of waste water could be carried out successfully at low operating pressures (250 psig).

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