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

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To cite this Article Sastri, V. S. and Ashbrook, A. W.(1976) 'Performance of Some Reverse Osmosis Membranes and Their Application in the Separation of Metals in Acid Mine-Water', Separation Science and Technology, 11: 2, 133 — 146

To link to this Article: DOI: 10.1080/01496397608085307

URL: http://dx.doi.org/10.1080/01496397608085307

SEPARATION SCIENCE, 11(2), pp. 133–146, 1976

Performance of Some Reverse Osmosis Membranes and Their Application in the Separation of Metals in Acid Mine-Water

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Abstract

Reverse osmosis separation behavior of some metal salts of Cu^{2+}, Ni^{2+}, Fe^{3+}, and Al^{3+} have been studied. The cellulose acetate membranes used 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. The importance of the chemical species present in solution and its effect on the degree of separation has been illustrated. Correlation between the percent solute separation and the equilibrium constant for the formation of ion-pairs in solution has been established. Reverse osmosis treatment has been applied to an acid mine-water solution, and the suitability of this process is discussed.

INTRODUCTION

The scope of reverse osmosis and its application for the treatment of electroplating waste solutions and acid mine drainage water have been discussed in a brief manner (*1*). Acid mine drainage water is a significant source of pollution of rivers and streams. Aerial and bacterial oxidation of sulfur results in the production of sulfuric acid which dissolves significant amounts of iron, calcium, and magnesium. Therefore, the treatment of acid mine-water is of practical interest from the points of view of both water pollution control and waste recovery. Even in low concentrations, some metal ions, such as copper and nickel, are toxic to fish and waste-water microorganisms (*2*, *3*). The application of reverse osmosis to such problem areas can help both to reduce water pollution and to produce product water which can be used in recycling operations.

Reverse osmosis operation at low pressures is of particular interest in waste-water treatment because of the possible reduction in capital investment vis-a-vis high-pressure systems, and in mechanical and membrane compaction problems. Recently an improved class of porous cellulose acetate membranes, having significantly high productivities at operating pressures of 300 psig or less, have been developed (*4*). This paper illustrates the performance of the Batch 316-type porous cellulose acetate membranes for the low-pressure treatment of acid mine drainage water solutions.

EXPERIMENTAL

Flow-Type Apparatus

Figures 1 and 2 illustrate the cell and the flow diagram of the apparatus used. The cell (Fig. 1), made of 310 stainless steel, consisted of two detachable parts. The upper part was a high-pressure chamber provided with the inlet and outlet openings for the flow of the feed solution under pressure. The lower part provided for the membrane support, with an outlet opening for the withdrawal of the membrane-permeated product solution. The preshrunk membrane was mounted on a porous stainless steel plate embedded in the lower part of the cell, which gave an effective area of membrane surface in the cell of 13.2 cm^2. The upper and the lower parts of the cell were set in proper alignment with rubber O-ring contacts between

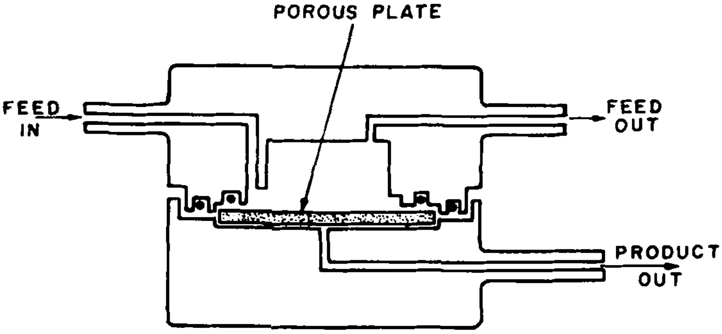

FIG. 1. Flow-type cell.

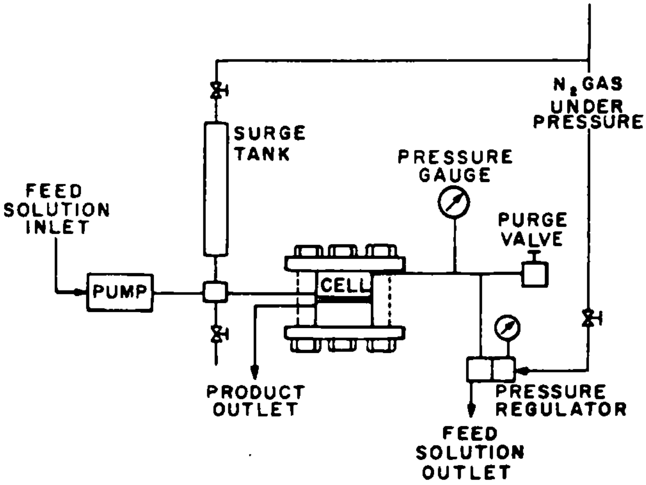

Fig. 2. Schematic diagram for flow-type apparatus.

the high-pressure chamber and the membrane. A pressure-tight joint was obtained by clamping the cell tightly between two thick end-plates. As shown in the flow diagram (Fig. 2), a high-pressure pump was used, and 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 operation the fluid pressure in the cell was indicated by a liquid-sealed pressure gauge. A stainless steel pressure regulator was used to maintain a constant operating pressure in the cell. The purge valve was used to drain the system whenever necessary. Nitrogen gas under pressure was used to load the dome of the Grove pressure regulator. 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 work. Six cells were used in series (one cell is illustrated in Fig. 2) so that six different membranes could be tested simultaneously.

PROCEDURE

All the experiments were carried out at the laboratory temperature (23 to 25 °C). The membranes, preshrunk under water at different temperatures (Table 2), were initially subjected to a pure water pressure of 350

TABLE 1

Film Casting Conditions

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

psig for 1 to 2 hr before subsequent use in reverse osmosis experiments at an operating pressure of 250 psig. In each experiment the pure water permeation rate, the membrane-permeated product rate per given area of film 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 specification and to specify the mass transfer coefficient on the high-pressure side of the membrane. The concentrations of sodium chloride in the feed and the product solutions were determined by specific resistance

TABLE 2

Membrane Specification and Performance Data[a]

				Feed concentration: 3500 mg/l NaCl, $k = 37.45 \times 10^{-4}$	
Film no.	Film shrinkage temp (°C)	$A \times 10^6$ (g—mole H_2O cm^2-sec-atm)	D_{AM}/K_δ for NaCl × 10^5 cm/sec	Solute separation(%)	Product rate (gpd/ft^2)
1	82	1.64	1.61	95.8	8.79
2	80	2.29	4.38	91.9	12.22
3	78.5	2.82	8.12	87.4	14.96
4	76	4.16	28.8	74.3	22.84
5	72	5.76	94.7	52.1	32.88
6	75.5	3.93	37.6	65.9	21.72

[a] Film type: Batch 316. Operating pressure: 250 psig. Feed solution: aqueous sodium chloride.

measurements. The feed and the product solutions containing calcium, copper, aluminum, iron, nickel, and lead were analyzed by atomic absorption spectrophotometry. The product rate data reported are accurate to within 3 %. Defining solute concentration c_A as weight of solute W_s divided by weight of solvent water W_w, the data on solute separation f were calculated from the relation

$$f = c_{A_1} - (c_{A_3}/c_{A_1}) \tag{1}$$

where subscripts 1 and 3 refer to the bulk solution on the high-pressure side of the membrane and the product solution on the atmospheric pressure side of the membrane, respectively. Because low metal ion concentrations are involved, the values of f are essentially the same as those obtained from the relation

$$f = \frac{\text{solute conc in feed} - \text{solute conc in product}}{\text{solute conc in feed}} \tag{2}$$

RESULTS AND DISCUSSION

Specifications of Membranes and Feed Flow Conditions

Reverse osmosis membranes can be characterized in terms of the pure water permeability constant, A, and solute transport parameter, $D_{AM}/K\delta$, at a given 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 experiment. Using the experimental pure water permeation rate, membrane permeated product rate, and solute separation data at preset operating conditions for the aqueous sodium chloride feed system containing 3500 mg/l salt, the values of A, $D_{AM}/K\delta$, and k were calculated by a computer program. The data on A and $D_{AM}/K\delta$ for sodium chloride at a pressure of 250 psig, given in Table 2, specify the films used in this work. The feed flow conditions used in all the reverse osmosis experiments carried out in the present work are specified in terms of the corresponding values of k obtained for the reference aqueous sodium chloride solution system containing 3500 mg/l of salt.

In order to compare the relative performance of different membranes for feed solution systems for which osmotic pressure and other physicochemical data are not readily available, it is necessary to provide such specifications for membranes and the feed flow conditions used in terms of parameters easily obtainable for a convenient reference feed solution system such as an aqueous sodium chloride solution.

The data given in Table 2 also serve to illustrate the high productivity of Batch 316-type membranes for reverse osmosis separation at low operating pressures.

Data on Solute Transport Parameter for Various Electrolytic Solutes

The values of diffusivity (D_{AB}) in cm^2/sec of the various electrolytic solutes in dilute aqueous solutions were obtained from the Nernst equation:

$$D_{AB} = \frac{\left(\dfrac{1}{Z_+} + \dfrac{1}{Z_-}\right)RT}{\left(\dfrac{1}{\lambda_+^\circ} + \dfrac{1}{\lambda_-^\circ}\right)F^2} \tag{3}$$

where Z_+ and Z_- are the valencies of cation and anion respectively, R is the gas constant (8.314 J°K^{-1} mole^{-1}), T is the absolute temperature, λ_+° and λ_-° are the limiting ionic conductances, (ohm^{-1} cm^2 equiv^{-1}), and F is the Faraday. For all the solutes studied in the present work, the values of λ_+°, λ_-°, and D_{AB} calculated from the above equation, and the values of mass transfer coefficient, k, calculated from:

$$k = k_{\text{ref}}\left[\frac{D_{AB}}{(D_{AB})_{\text{ref}}}\right]^{2/3} \tag{4}$$

TABLE 3

List of Solutes Used with Some Physicochemical Data

No.	Solute	λ_+°	λ_-°	$D_{AB} \times 10^5$ (cm^2/sec)	$k \times 10^4$ (cm/sec)
1	$CuSO_4$	55.0	80.8	0.8709	24.86
2	$Cu(NO_3)_2$	55.0	71.42	1.2403	31.47
3	$NiSO_4$	50.5	80.8	0.8270	24.04
4	$Ni(NO_3)_2$	50.5	71.42	1.181	30.46
5	$NiCl_2$	50.5	76.44	1.214	31.03
6	$Fe_2(SO_4)_3$	68.4	80.8	0.8215	23.93
7	$Fe(NO_3)_3$	68.4	71.42	1.240	31.46
8	$Al_2(SO_4)_3$	61.0	80.80	0.2438	10.64
9	$Al(NO_3)_3$	61.0	71.42	1.233	31.35

are given in Table 3. In Eq. (4), k_{ref} is the mass transfer coefficient on the high-pressure side of the membrane for the reference solution system of 3500 ppm aqueous sodium chloride (37.45×10^{-4} cm/sec), and $(D_{AB})_{\text{ref}}$ and D_{AB} refer to the diffusivity of sodium chloride and the salt under consideration, respectively.

Using the experimental data on solute separation (f) and product rate (PR), the values of solute transport parameter for every solute for the different membranes were calculated from the equation:

$$D_{AM}/K_{\delta} = \frac{(\text{PR})}{3600Sd}\frac{1-f}{f}\left[\exp\frac{(\text{PR})}{3600Kd}\right]^{-1} \tag{5}$$

where S is the effective membrane area (13.2 cm^2), k is the mass transfer coefficient on the high-pressure side of the membrane, and d is the density of the solution. The resulting values of D_{AM}/K_{δ} together with the values of degree of separation and product rates are presented in Table 4.

The values of the solute transport parameter for any single solute vary among the six films used in the reverse osmosis experiment. The data show that the values of D_{AM}/K_{δ} increase with a decrease in the percent solute separation and with an increase in product rate values.

Separation of Different Salts

Data on the percent solute separation, together with the product rates (in gal ft^{-2} day^{-1}) for the various solutes [$CuSO_4$, $Cu(NO_3)_2$, $NiSO_4$,

TABLE 4

Data on Solute Transport Parameters

Solute	Separation	Product rate	k (cm/sec)	D_{AM}/K_{δ} (cm/sec)
$CuSO_4$	0.9904	23.12	24.86×10^{-4}	4.715×10^{-6}
	0.9971	32.0		1.958×10^{-6}
	0.9943	38.9		4.691×10^{-6}
	0.9774	56.74		2.759×10^{-5}
	0.9443	77.00		9.550×10^{-5}
	0.9648	53.28		4.088×10^{-5}
$Cu(NO_3)_2$	0.9431	24.86	31.47×10^{-4}	3.156×10^{-5}
	0.9092	34.67		7.284×10^{-5}
	0.8608	42.23		1.437×10^{-4}
	0.8185	58.60		2.733×10^{-4}
	0.6708	77.63		8.012×10^{-4}
	0.7392	55.12		4.090×10^{-4}

(*continued*)

TABLE 4 (continued)

Solute	Separation	Product rate	k (cm/sec)	D_{AM}/K_δ (cm/sec)
$NiSO_4$	0.9956	24.26	24.04×10^{-4}	2.256×10^{-5}
	0.9960	33.48		2.828×10^{-5}
	0.9950	40.59		4.290×10^{-5}
	0.9840	57.46		1.965×10^{-4}
	0.9487	78.73		8.957×10^{-4}
	0.9577	54.88		5.098×10^{-4}
$Ni(NO_3)_2$	0.9738	23.47	30.46×10^{-4}	1.329×10^{-5}
	0.9712	32.32		2.016×10^{-5}
	0.9571	39.27		3.703×10^{-5}
	0.8828	56.82		1.587×10^{-5}
	0.7470	77.14		5.494×10^{-4}
	0.8167	53.50		2.526×10^{-4}
$NiCl_2$	0.9797	23.51	31.03×10^{-4}	1.025×10^{-5}
	0.9785	32.41		1.498×10^{-5}
	0.9681	39.35		2.728×10^{-5}
	0.9129	56.91		1.142×10^{-4}
	0.8025	77.07		3.989×10^{-4}
	0.8544	53.54		1.919×10^{-4}
$Fe_2(SO_4)_3$	0.9961	23.70	23.93×10^{-4}	1.952×10^{-5}
	0.9928	32.66		4.983×10^{-5}
	0.9867	39.23		1.112×10^{-4}
	0.9887	53.92		1.296×10^{-4}
	0.9596	69.16		6.122×10^{-4}
	0.9723	49.84		2.986×10^{-4}
$Fe(NO_3)_3$	0.9848	24.20	31.46×10^{-4}	7.859×10^{-6}
	0.9798	33.76		1.464×10^{-5}
	0.9700	40.73		2.650×10^{-5}
	0.9479	56.91		6.579×10^{-5}
	0.9000	73.12		1.709×10^{-4}
	0.9197	52.73		9.684×10^{-5}
$Al_2(SO_4)_3$	0.9980	25.65	10.64×10^{-4}	1.081×10^{-5}
	0.9960	35.45		2.993×10^{-5}
	0.9723	42.41		2.540×10^{-4}
	0.9338	59.34		8.839×10^{-4}
	0.9453	71.32		8.669×10^{-4}
	0.8000	53.72		2.822×10^{-3}
$Al(NO_3)_3$	0.9829	25.44	31.35×10^{-4}	9.312×10^{-6}
	0.9657	35.37		2.643×10^{-5}
	0.9529	42.45		4.414×10^{-5}
	0.9304	59.48		9.359×10^{-5}
	0.8887	76.61		2.018×10^{-4}
	0.9069	54.55		1.178×10^{-4}

TABLE 5

Data on Solute Separation

	Film 1		Film 2		Film 3		Film 4		Film 5		Film 6	
Salt (ppm)	% Solute separation	Product rate[a]	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate	% Solute separation	Product rate
$CuSO_4$ (109)	98.07	10.78	>99.54	14.96	99.45	18.24	98.62	26.52	95.69	36.21	97.52	24.91
$CuSO_4$ (224)	97.86	10.81	99.33	14.96	99.33	18.18	98.30	26.39	95.09	35.76	96.83	24.74
$CuSO_4$ (260)	—	10.62	99.51	14.72	99.39	17.93	97.89	26.11	95.29	35.60	96.15	24.62
$CuSO_4$ (1220)	99.04	10.31	99.71	14.28	99.43	17.36	97.74	25.31	94.43	34.36	96.48	23.77
$CuSO_4$ (1370)	98.94	10.78	99.64	14.91	99.30	18.11	97.52	26.43	93.94	36.06	95.36	24.74
$Cu(NO_3)_2$ (1300)	94.31	11.09	90.92	15.4	86.08	18.84	81.85	26.14	67.08	34.64	73.92	24.60
$NiSO_4$ (53)	98.11	10.81	99.06	14.98	99.25	18.25	99.06	26.49	97.74	35.99	98.49	24.91
$NiSO_4$ (60)	—	10.94	98.17	15.11	98.30	18.35	97.50	26.67	97.50	36.18	97.67	25.06
$NiSO_4$ (1170)	99.56	10.82	99.60	14.94	99.50	18.11	98.40	25.64	94.87	35.14	95.77	24.48
$NiSO_4$ (1220)	99.55	10.65	99.65	14.68	99.56	17.80	98.36	25.75	95.29	34.64	96.11	24.04
$NiSO_4$ (2515)	99.21	10.49	—	14.48	99.30	17.56	97.32	25.64	93.44	34.45	95.33	24.02
$NiCl_2$ (838)	97.97	10.49	97.85	14.45	96.81	17.56	91.29	25.39	80.25	34.39	85.44	23.89
$Ni(NO_3)_2$ (1181)	97.38	10.47	97.12	14.42	95.71	17.52	88.28	25.35	74.70	34.42	81.67	23.87
$Fe_2(SO_4)_3$ (60)	>98.33	11.74	>98.33	16.24	>98.33	19.65	>98.33	26.70	98.06	34.90	98.06	24.85
$Fe_2(SO_4)_3$ (1950)	99.61	10.57	99.28	14.57	98.67	17.50	98.87	24.02	95.96	30.86	97.23	22.24
$Fe(NO_3)_3$ (1179)	98.48	10.80	97.98	15.06	97.00	18.18	94.79	25.39	90.00	32.62	91.97	23.53
$Al_2(SO_4)_3$ (1480)	99.80	11.45	99.60	15.81	97.23	18.92	93.38	26.48	94.53	31.82	80.00	23.97
$Al(NO_3)_3$ (934)	98.29	11.35	96.57	15.79	95.29	18.94	93.04	26.55	88.87	34.18	90.69	24.34

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

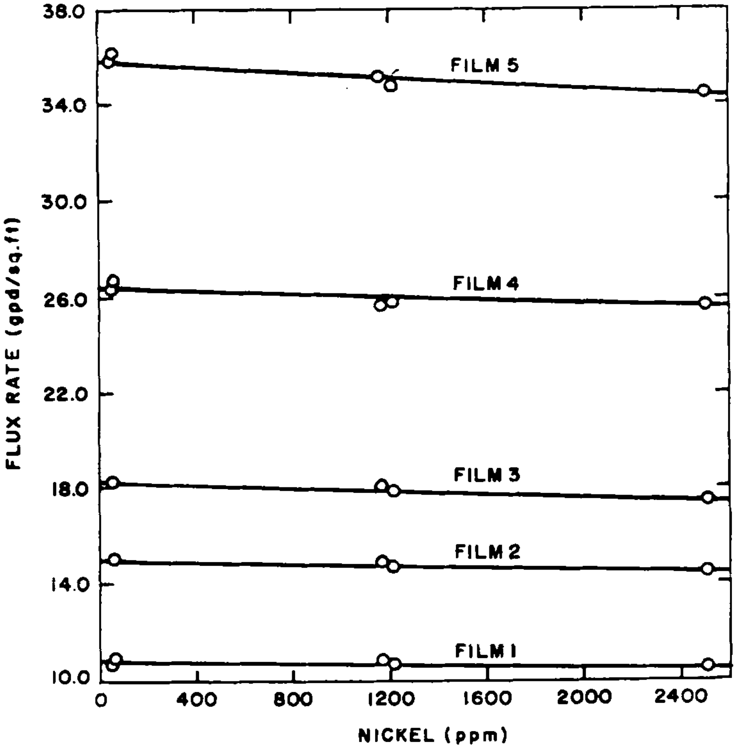

FIG. 3. Effect of nickel ion concentration on flux rate.

$NiCl_2$, $Ni(NO_3)_2$, $Fe_2(SO_4)_3$, $Al(NO_3)_3$] are presented in Table 5. The concentration of the metal salt in the case of copper and nickel was varied to determine the effect of the feed concentration on the degree of separation. The effect of variation of the concentration of nickel sulfate in the feed solution on the flux rate is depicted in Fig. 3. It is clear from this figure that the drop in flux rate is insignificant in the range of 11.0 to 26.0 gal ft^{-2} day^{-1} up to a feed concentration of 2500 ppm of nickel sulfate.

Data on the degree of solute separation as a function of the concentration of nickel sulfate in the feed solution are plotted in Fig. 4. Solute separation of the order 99% and greater can be obtained up to a concentration of 2500 ppm of nickel sulfate. These values of solute separation correspond to a maximum product rate of 18.0 gal ft^{-2} day^{-1}. Thus it can be seen from the data given in Table 5 that Films 1, 2, and 3 are

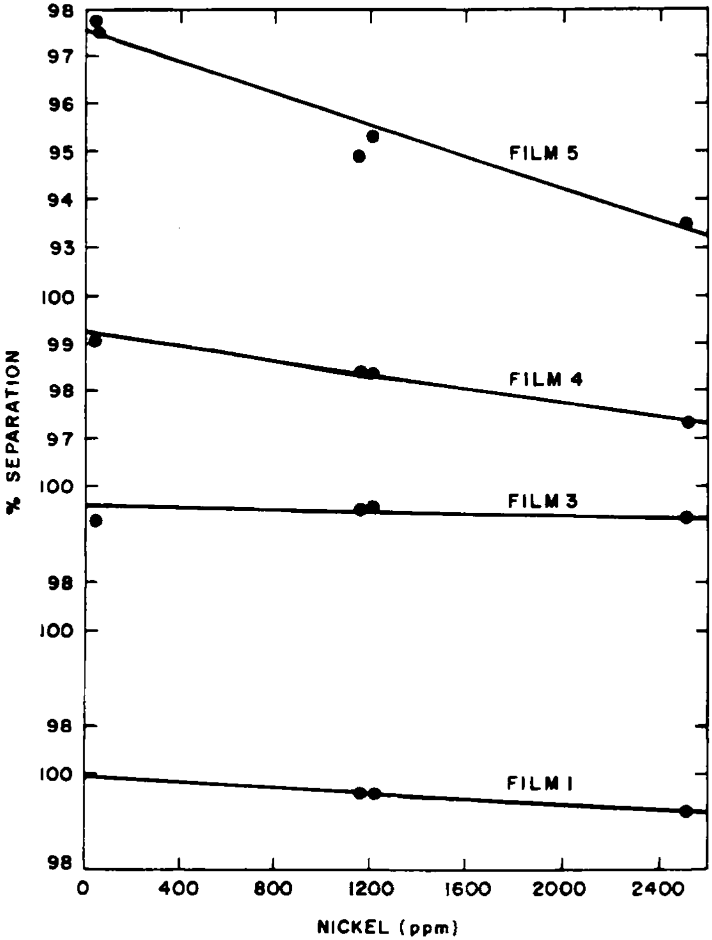

FIG. 4. Effect of nickel ion concentration on percent separation.

adequate for the purpose of separation of metal ions of the order of 99 to 100%.

Comparison of the solute separation data (Table 5) in the case of Films 1 and 5 shows that the degree of separation increases in going from sodium chloride through copper sulfate to ferric sulfate. Thus cations of higher charge are separated better than cations of lower charge, and the order of separation is $M^{3+} > M^{2+} > M^{+}$. It is also interesting to compare the solute separation data obtained in the case of salts having the same cation but associated with different anions. For example, the percent solute separation of $CuSO_4$ is greater than of $Cu(NO_3)_2$ for the same film. The same trend holds in the case of other salts—$Fe_2(SO_4)_3 > Fe(NO_3)_3$ and $Al_2(SO_4)_3 > Al(NO_3)_3$.

In Fig. 5 the solute separation data for $Ni(NO_3)_2$, $NiCl_2$, and $NiSO_4$ are plotted as a function of log K_{ip}, where K_{ip} is the equilibrium constant

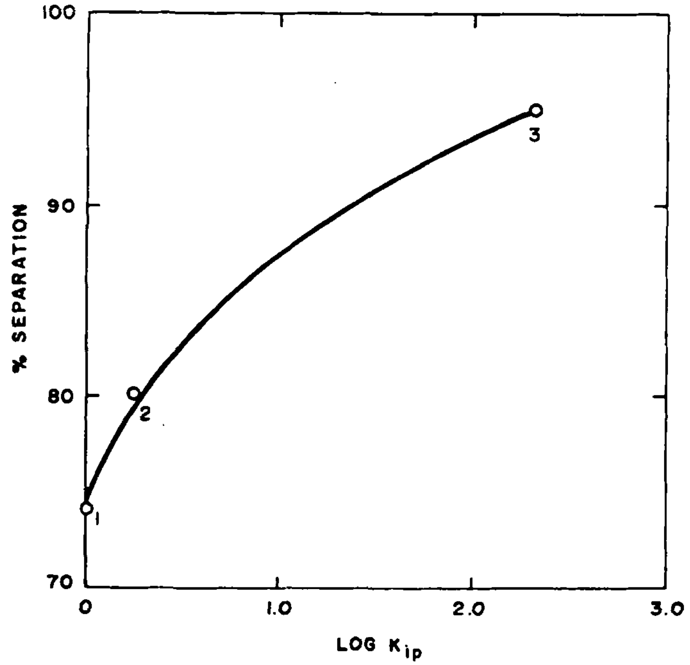

FIG. 5. Correlation of percent separation with ion-pair equilibrium constant.

TABLE 6

Data on Separation of Metal Ions in Acid Mine-Water

	Metal ion (ppm)[a]						Product rate
	Ca^{2+}	Cu^{2+}	Al^{3+}	Fe^{3+}	Ni^{2+}	Pb^{2+}	
Acid mine-water feed	323	15	9	14	<0.1	1.8	—
Product water,							
Film 1	4	0.3	<1	<0.1	Nil	<0.5	11.31
Film 2	8	0.5	<1	0.2	Nil	<0.5	15.55
Film 3	13	0.5	<1	0.2	Nil	<0.5	18.98
Film 4	17	0.5	<1	0.3	Nil	<0.5	26.48
Film 5	43	1.7	<1	1.0	Nil	<0.5	32.10
Film 6	30	1.1	<1	0.8	Nil	<0.5	24.00

[a] Analysis by atomic absorption spectrophotometry.

for the formation of the ion-pair

$$Ni^{2+} + X^- \leftrightarrows Ni^{2+}X^-$$

It is evident from this figure that the percent separation of the solute increases with increasing value of the ion-pair equilibrium constant. Thus it is apparent that the chemical species present in solution is of importance in the separation of metal ions by reverse osmosis. The cellulose acetate membranes have proton affinity and, in the case of an ion-pair, both the size and the effective charge may prevent the approach of the ion-pair toward the surface layer of the membrane. As a result, the ion-pair is separated better than the hydrated cation. It is appropriate to point out that treatment of a solution containing several anions (e.g., SO_4^{2-}, Cl^-, NO_3^-) and some cations (e.g., Cu^{2+}, Fe^{3+}) by reverse osmosis would result in a separation in keeping with the concentrations of ion-pairs and bare hydrated metal ions.

The results obtained from the treatment of acid mine-water (Elliot Lake, Ontario, Canada) by reverse osmosis are presented in Table 6. The analytical data show that Film 1 gave the best separation of metal ions with a product rate of 11.31 gal ft^{-2} day^{-1}. The predominant anion in the mine-water sample is sulfate, and hence there must be a significant amount of ion-pairs in solution. Reference to Tables 6 and 2 shows that the degree of separation of metal ions is in keeping with the membrane specification and performance data. It can be concluded from these data that if the film shrinkage temperature is high and A and D_{AM}/K_δ are small, then good metal separation can be obtained.

REFERENCES

1. V. S. Sastri, Canada, Department of Energy, Mines and Resources, Canada Centre for Minerals and Energy Technology, Ottawa, Scientific Bulletin No. CM 75–7 (1975).
2. J. R. E. Jones, *Fish and Water Pollution*, Butterworths, London, (1964).
3. G. W. Malaney, *Sewage Ind. Wastes*, *31*, 1309 (1959).
4. B. Kunst and S. Sourirajan, *J. Appl. Polym Sci.*, *14*, 723, 1983, 2559 (1970).

Received by editor July 11, 1975