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Reverse Osmosis Separation of Metal Ions in Acid Mine-Water

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Abstract

Cellulose acetate membranes obtained from Osmonics Inc. were characterized in terms of pure water permeability constant, solute transport parameter, and mass transfer coefficient with the reference system of aqueous sodium chloride solution. Reverse osmosis separation behavior of Ca, Mg, Zn, Mn, Cu, Al, and Fe as nitrate, chloride, and sulfate salts was studied. The effect of the addition of sodium sulfate to $Mg(ClO_4)_2$ and $Mn(NO_3)_2$ solutions on solute separation was also investigated. Acid mine-water obtained from New Brunswick was subjected to reverse osmosis, and separation of metal ions in the range of 95 to 99% was obtained along with the recovery of product water of suitable quality for use in recycle operations.

INTRODUCTION

During the past few years the problem of wastewater disposal from the base metal mining industry, principally in New Brunswick and the Yukon and Northwest Territories, has been studied by some government agencies. The pollution problems associated with the mining industry are not very well known to the public because of the fact that the mining operations take place in locations which are remote from densely populated areas. However, it should be pointed out that pollution by mine wastewater discharges is receiving considerable attention and this paper is concerned with the treatment of mine discharges by reverse osmosis in order to obtain product water of suitable quality either for recycling purpose or for discharge into nearby streams.

The wastewaters from base metal mining operations can be separated into two distinct types: (a) acid mine drainage and (b) tailings pond discharges. This classification is based on the physical and chemical characteristics of the wastewaters. The origin of these two types of wastewaters appears to be related to the high pyrite content of the ore. The typical characteristics of acid mine drainage wastewater are low pH; generally high amounts of heavy metal ions such as iron, zinc, copper, and lead; a high concentration of dissolved solids; and a negligible amount of organic contaminants. The two pollutants in acid mine-water, acidic pH and the heavy metal ion content, have been shown to be toxic to aquatic life (*1–3*).

Acid mine drainage is normally generated in underground mining operations through either chemical or bacteriological mechanisms or a combination of both. This type of wastewater may also be obtained from tailings dam seepage, from runoff from ore piles, waste rock dumps, dried exposed tailings, and from the mine property itself containing exposed sulfide minerals. The mechanism of generation of acid from pyrite has been extensively studied (*4*, *5*).

Reverse osmosis is a promising method for desalinization and concentration of aqueous salt solutions, and the process does not involve any phase transformation of the liquid. Some of the attractive features of reverse osmosis are low expenditure of energy, simplicity of processing technology, and the operation of the process at ambient temperatures. Reverse osmosis at high pressures suffers from the disadvantages of high capital investment and membrane compaction problems. On the other hand, low-pressure reverse osmosis involves lower capital investment and a negligible amount of membrane compaction. The work done so far on the low-pressure reverse osmosis treatment of metal-bearing waste effluents (*6–12*) has been encouraging in that both valuable metal ions and product water of reasonable quality could be recovered at the same time. For these reasons a detailed study of the reverse osmosis treatment of metal ions encountered in acid mine drainage which occurs in New Brunswick under a variety of conditions was undertaken.

EXPERIMENTAL

Static Cell Set-up

The stainless steel static cell consisted of two detachable parts, and the membrane was supported by a stainless steel porous plate embedded in the lower part of the cell. The lower part of the cell was provided with an outlet through which the membrane permeated product solution was collected at atmospheric pressure. The upper part of the cell contained the feed solution of interest under pressure in contact with the membrane. The two parts of the static cell were fitted and sealed with the aid of two rubber O-rings. The effective surface area of the membrane in the cell was 13.4 cm^2. The desired pressure was achieved by compressed nitrogen gas from a gas cylinder. A magnetic stirrer fitted in the upper part of the cell, located about 0.64 cm above the membrane, was used in the uniform stirring of the feed solution, and this minimized the concentration polarization. The schematic diagram of the whole experimental setup is similar to the one reported earlier (*9*). The cellulose acetate membranes used in the present studies were obtained from Osmonics Inc.

PROCEDURE

All the experiments were conducted at laboratory temperature (23 to 25°C). The membranes were pressurized with pure water at 400 psig for 2 hr before subsequent use in the experiments at the operating pressure of 300 psig. The pure water permeation rate (PWP), the membrane permeated product rate (PR) for a given area of the membrane, and the solute separation (f) were determined in all the experiments at preset operating conditions. A feed solution containing 1300 mg/l of sodium chloride was used to obtain data on membrane specification and to specify the mass transfer coefficient (k) on the high-pressure side of the membrane. The feed and the product solutions containing sodium chloride were analyzed by specific resistance measurements. The feed and the product solutions containing Fe, Cu, Zn, Ca, Mg, Mn, Ni, and Al were analyzed by atomic absorption spectrophotometry at wavelengths of 2483, 3248, 2139, 4227, 2852, 2795, 2320, and 3093 Å, respectively. The product rate data were corrected with respect to viscosity and the temperature (25°C). Because low metal ion concentrations were employed in the experiments, solute separation (f) data were calculated using the relation:

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

RESULTS AND DISCUSSION

Membrane Specifications

Reverse osmosis membranes can be specified in terms of parameters such as the pure water permeability constant, A, and the solute transport parameter, $D_{AM}/K\delta$, at a particular operating pressure. The product rate and the solute separation obtainable with a membrane so specified are functions of the mass transfer coefficient, k, on the high-pressure side of the membrane, which is governed by feed flow rate and the feed concentration used in the experiment. A computer program (*13*) using 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 1300 ppm salt was used in the calculation of A, $D_{AM}/K\delta$, and k. The data given in Table 1 on the values of A and $D_{AM}/K\delta$ for sodium chloride at 300 psig specify the membrane used in the present investigations. The feed flow conditions used in all the experiments done in the present studies are specified in terms of the corresponding value of k obtained with the reference sodium chloride containing 1300 ppm of salt. To enable comparison of the relative performance of the membrane for feed solutions for which physicochemical data such as osmotic pressure and other pertinent data are not readily available, it is useful to provide such specifications for the membrane in terms of easily obtainable parameters for a convenient and well-studied reference feed solution such as sodium chloride solution.

TABLE 1

Membrane Specification Data[a]

			Feed concentration, 1300 mg/l NaCl; $k = 10.89 \times 10^{-4}$ cm/sec	
Film no.	$A \times 10^6$ (g mole H_2O $cm^{-2}sec^{-1}atm^{-1}$)	$D_{AM}/K\delta \times 10^5$ (cm/sec)	Solute separation (%)	Product rate (g/hr)
1	2.82	10.93	76.60	32.20
1	2.73	13.74	75.77	31.88

[a] Membrane area, 13.4 cm^2; pressure, 300 psig.

Solute Transport Parameter

In Table 2 the solutes used in the present studies together with the relevant physicochemical data such as the limiting ionic conductances (λ_+, λ_-), the calculated diffusivities (D_{AB}), and the mass transfer coefficient (k) values are given. The analysis of the data and the relations used in the calculations are the same as reported earlier (*10*). Using the data on product rates (PR), solute separation (f), the effective membrane area (s), the density of the solution (d), and the mass transfer coefficient (k) values, the solute transport parameter (D_{AM}/K_δ) for the various solutes studied were calculated. The data on D_{AM}/K_δ and k, together with solute separation and product rates, are given in Table 3.

Separation of Various Salts

The solute separation data (Table 3) of the 20 metal salts studied show an increase in the separation in going from sodium chloride through

TABLE 2

List of Solutes Used with Some Physicochemical Data

No.	Solute	λ_+°	λ_-°	$D_{AB} \times 10^5$ (cm²/sec)	$k \times 10^4$ (cm/sec)
1	$NaCl$	50.11	76.44	1.610	10.890
2	$Ca(NO_3)_2$	59.50	71.42	1.296	9.424
3	$CaCl_2$	59.50	76.44	1.336	9.614
4	$Mg(ClO_4)_2$	53.06	67.30	1.184	8.873
5	$MgCl_2$	53.06	76.44	1.250	9.200
6	$MgSO_4$	53.06	80.80	0.852	7.125
7	$Zn(NO_3)_2$	54.10	71.42	1.229	9.095
8	$ZnCl_2$	54.10	76.44	1.264	9.267
9	$ZnSO_4$	54.10	80.80	0.862	7.182
10	$Mn(NO_3)_2$	53.50	71.42	1.222	9.061
11	$MnSO_4$	53.50	80.80	0.857	7.151
12	$Cu(NO_3)_2$	55.00	71.42	1.240	9.152
13	$CuCl_2$	55.00	76.44	1.445	10.133
14	$CuSO_4$	55.00	80.80	0.871	7.230
15	$Al(NO_3)_3$	61.00	71.42	1.233	9.116
16	$AlCl_3$	61.00	76.44	1.204	8.972
17	$Al_2(SO_4)_3$	61.00	80.80	0.244	3.094
18	$Fe(NO_3)_3$	68.40	71.42	1.240	9.150
19	$FeCl_3$	68.40	76.44	1.281	9.351
20	$Fe_2(SO_4)_3$	68.40	80.80	0.822	6.954

TABLE 3

Data on Solute Transport Parameters

Salt	Solute separation	Product rate (g/hr)	k (cm/sec) × 10^4	D_{AM}/K_δ (cm/sec) × 10^5
$Ca(NO_3)_2$	0.8738	29.28	9.424	8.765
$CaCl_2$	0.8947	28.69	9.614	6.999
$Mg(ClO_4)_2$	0.8600	27.79	8.873	9.377
$MgCl_2$	0.8930	25.84	9.200	6.418
$MgSO_4$	0.9609	27.88	7.125	2.351
$Zn(NO_3)_2$	0.8522	30.11	9.095	10.823
$ZnCl_2$	0.8679	29.44	9.267	9.288
$ZnSO_4$	0.9552	30.67	7.182	2.981
$Mn(NO_3)_2$	0.8738	30.09	9.061	9.007
$MnSO_4$	0.9376	31.05	7.151	4.282
$Cu(NO_3)_2$	0.9098	28.43	9.152	5.842
$CuCl_2$	0.9386	31.32	10.133	4.247
$CuSO_4$	0.9526	31.82	7.230	3.281
$Al(NO_3)_3$	0.9272	24.69	9.116	4.019
$AlCl_3$	0.9560	24.88	8.972	2.374
$Al_2(SO_4)_3$	0.9690	28.10	3.094	1.860
$Fe(NO_3)_3$	0.9713	29.69	9.150	1.818
$FeCl_3$	0.9889	28.48	9.351	0.663
$NH_4Fe_2(SO_4)_2$	0.9889	27.34	6.954	0.636

manganous sulfate to ferric sulfate. Metal salts of trivalent cations give the highest separation and the order of separation is $M^{3+} > M^{2+} > M^+$ where M represents a metal ion. It is to be noted that the solute transport parameter (D_{AM}/K_δ) decreased with an increase in the solute separation. It is also interesting to compare the solute separation data in the case of salts of the same metal ion associated with different anions. For example, the solute separation of $MgSO_4$ is greater than $MgCl_2$ which in turn is greater than $Mg(ClO_4)_2$. The same trend holds in the case of other salts—$CaCl_2 > Ca(NO_3)_2$; $ZnSO_4 > ZnCl_2 > Zn(NO_3)_2$; $MnSO_4 > Mn(NO_3)_2$; $CuSO_4 > CuCl_2 > Cu(NO_3)_2$; $Al_2(SO_4)_3 > AlCl_3 > Al(NO_3)_3$; and $Fe_2(SO_4)_3 > Fe(NO_3)_3$. The observed increase in solute separation in the case of metal sulfates—as compared to that of metal nitrates—may be attributed to the presence of the metal ion sulfate ion-pairs in solution.

In order to understand the role of ion-pair species in the solute separation by reverse osmosis, the separations of magnesium perchlorate (1000 ppm Mg) and manganous nitrate (1000 ppm Mn) in the presence of added sodium sulfate (0 to 1000 ppm) were studied. The results obtained from these experiments are depicted in Figs. 1 and 2. The addition of 1000 ppm sodium sulfate to manganous nitrate (1000 ppm Mn) resulted in increasing the solute separation from 89.1 to 91.6% (Fig. 1). In the case of magnesium perchlorate (1000 ppm Mg), the addition of 1000 ppm sodium sulfate increased the separation of magnesium from 87.1 to

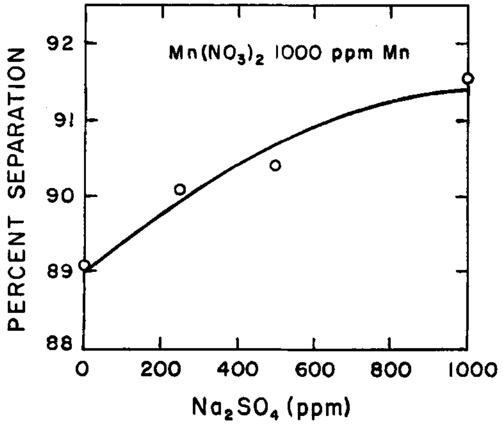

FIG. 1. Effect of Na_2SO_4 on the separation of manganese at 300 psig.

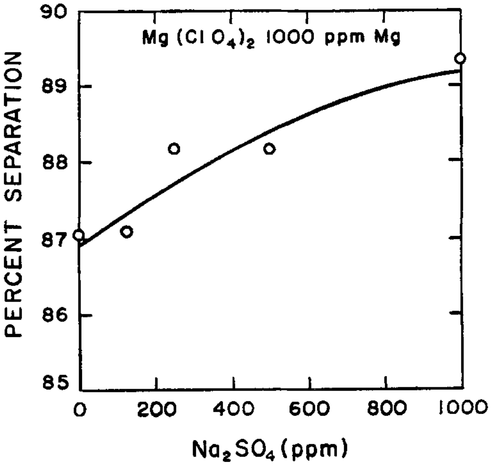

FIG. 2. Effect of Na_2SO_4 on the separation of magnesium at 300 psig.

89.4% (Fig. 2). The observed increase in the separation of manganese and magnesium in the presence of added sodium sulfate may be attributed to the formation of ion-paired species in solution ($M^{2+}SO_4^{2-}$) which are separated better than aquo metal ions such as manganese or magnesium. Recently Sourirajan and co-workers (*14*) have published their studies on the reverse osmosis separation of several metal salts and concluded that for cellulose acetate membranes, the general effect of ion-pair formation is to increase the solute transport parameter, D_{AM}/K_δ, and hence decrease solute separation in reverse osmosis. The data presented in Table 5 by Sourirajan (*14*) show that for Films 3, 4, and 5 both the calculated and experimental values of solute separation are higher at 0.51 *m* as compared to 0.02 *m* of magnesium sulfate solution. It is an established fact that in a 0.51 *m* solution of magnesium sulfate there is a considerable amount of ion-pairs in solution as compared to a 0.02 *m* solution. Thus it is logical to conclude from these data that the effect of ion-pairs on reverse osmosis separation is to increase the solute separation. This effect of ion-pairs on solute separation has been found to hold good in the case of zinc and nickel sulfate solutions as well (*10*, *11*).

Ion-pair formation in the case of metal ion sulfate solutions and the resulting increase in solute separation is of significance in practical situations. In the case of solutions containing metal ions associated with either nitrate or chloride anion, it is possible to increase the solute separation by the addition of sodium sulfate and at the same time obtain high product water recovery by using more porous cellulose acetate membranes. Ion-pair formation and the consequent increase in solute separation can be considered significant for the practical industrial treatment of barren mining and metallurgical waste effluents containing trace amounts of metal ions associated with nitrate, chloride, or perchlorate anion.

Acid mine-water sample obtained from New Brunswick (Canada) mining operations was subjected to reverse osmosis treatment, and the results obtained from the experiments are presented in Table 4. Comparison of the data on the metal ion concentrations in the feed and the product water shows that the separation of metal ions is in the range of 95 to 99% with a product rate of 26.2 g/hr for an effective surface area of 13.4 cm^2. The degree of separation of the metal salts and the product rate are in keeping with the membrane specifications and the feed flow conditions (Table 1). The predominant anion in the mine-water feed solution is sulfate ion, and hence it is reasonable to expect the presence of significant amounts of ion-pairs involving the various cations. From these data (Table 4) it is clear that the product water is of suitable quality

TABLE 4

Data on Separation of Metal Ions in Acid Mine-Water[a]

Acid mine-water	Metal ion (ppm)								Product rate (g/hr)
	Fe	Cu	Zn	Ca	Mg	Mn	Ni	Al	
Feed	780	220	220	150	300	63	2	370	—
Product water	10	11	3	2	4	0.9	0.03	3	26.20

[a] Membrane area, 13.4 cm^2; pressure, 300 psig.

for use in recycling operations. It may be necessary to subject the product water to a second-stage reverse osmosis treatment to produce product water which meets the environmental standards for discharge into nearby streams.

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