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Reverse Osmosis Separation of Nickel from Dilute Solutions*

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Abstract

Cellulose acetate membranes were characterized in terms of the pure water permeability constant, the solute transport parameter, the mass transfer coefficient, and percent solute separation using a reference system of aqueous sodium chloride solution. The membranes were used in the determination of reverse osmosis characteristics such as product rates and solute separation of dilute nickel salt solutions. The effect of the chemical species present in aqueous nickel salt solution on the degree of separation of nickel has been determined. The results of this study can be used in predicting the general reverse osmosis separation behavior of metals such as Zn, Cu, Pb, Mg, and Mn encountered in acid mine-water samples.

INTRODUCTION

A brief discussion of the principles of reverse osmosis, the physicochemical criteria for the separation of metal ions, and the various factors governing the stability of cellulose acetate membranes in the reverse osmosis treatment of metal ion-bearing waste solutions has been published recently (*1*, *2*). 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 were applied with success in the treatment of a sample of acid mine-water (*3*). Low-pressure reverse osmosis treatment of dilute uranium and zinc solutions using cellulose acetate membranes has been reported (*4*, *5*). The results obtained so far from the studies on low-pressure reverse osmosis treatment of heavy

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metal-bearing effluents are promising in that both heavy metals and pure product water could be recovered at the same time.

In the metal plating industry, the major pollution problem arises from the toxicity of the chemicals involved and the large volumes of water used in the rinsing operations. This results in a significant loss of economically valuable chemicals. Therefore, the treatment of rinse waters from metal-finishing plants is of practical interest from the points of view of both water pollution control and waste recovery. This is particularly so in the case of nickel-plating wastewater. Even in low concentrations, nickel is toxic to fish and wastewater microorganisms (*6*, *7*). The discharge of nickel-bearing effluents into municipal wastewater results in water pollution, loss of valuable nickel, and a reduction in the efficiency of the biological treatment processes (*8*, *9*). The application of reverse osmosis for the treatment of waste solutions containing nickel can help reduce water pollution and recover the valuable nickel. Nickel-plating solutions and rinse water from nickel-plating baths usually have a pH in the range of 4 to 6. Cellulose acetate membranes are stable with respect to hydrolysis in the pH range of 3 to 7. Thus the nickel-bearing waste solutions are particularly amenable to reverse osmosis treatment at the laboratory temperature (25°C) using the commercially available porous cellulose acetate membranes.

Reverse osmosis is one of the most promising methods for desalinization and concentration of aqueous salt solutions and does not involve any phase transformation of the liquid. Low expenditure of energy, simplicity of the processing technology, and the operation of the process at 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 unattractive. The reverse osmosis treatment of metal ion-bearing effluents at low pressures ($\simeq 300$ psig) can result in the recovery of the valuable metal ions and the production of water that can be either discharged into streams or used in recycling operations. For these reasons, a systematic and detailed study of the reverse osmosis behavior of nickel salt solutions under a variety of experimental conditions was undertaken.

EXPERIMENTAL

Nonflow Type Cell

The schematic diagram of the nonflow type experimental arrangement is the same as reported earlier (*4*). The static cell 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 collected at atmospheric pressure from an outlet provided in the lower part of the cell. The upper 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 means of two rubber O-rings. The effective area of the membrane surface in the cell was 11.4 cm^2. Compressed nitrogen gas from a gas cylinder was used in achieving the desired degree of pressurization. During the course of the experiment, the feed solution was stirred by a magnetic stirrer fitted in the cell about 0.64 cm above the membrane, and this resulted in minimizing the concentration polarization. Cellulose acetate membranes obtained from Osmonics Inc. were used in the present work.

PROCEDURE

All the reverse osmosis experiments were carried out at the laboratory temperature (23 to 25 °C). The porous cellulose acetate membranes were subjected to pressurization with pure water at 400 psig for about 2 hr before subsequent use in the reverse osmosis experiments at operating pressures of 100 to 300 psig. In all the experiments, the pure water permeation rate, the membrane permeated product rate for a given surface area of the membrane, and the percent solute separation (f) were determined at preset operating conditions. Feed solutions containing sodium chloride at a concentration of 1500 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 sodium chloride concentrations in the feed and the membrane permeated product solutions were determined by specific resistance measurements. The feed and product solutions containing nickel ion were analyzed by atomic absorption spectrophotometry at a wavelength of 2320 Å and slit width of 50 μm. The product rate data reported are corrected with respect to the viscosity and the temperature (25 °C). The product rate data are accurate to within 3 %. Because low metal ion concentrations are involved, the values of f are calculated from the relation

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

RESULTS AND DISCUSSION

Specifications of Membranes

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_δ, at a particular value of the operating pressure. The flux or the product rate and the solute separation obtainable with the membrane so specified are functions of the mass transfer coefficient, k, on the high-pressure side of the membrane, which is governed by the feed flow-rate and the concentration of the feed solution used in the experiment. Experimental data on the pure water permeation rate, membrane permeated product rate (flux), and solute separation at preset operating conditions for the reference aqueous sodium chloride feed solution containing 1500 mg/l salt were used in the calculation of the pure water permeability constant (A), the solute transport parameter (D_{AM}/K_δ), and the mass transfer coefficient (k) by means of a computer program (*10*). The data on the values of A and D_{AM}/K_δ for sodium chloride at 300 psig are presented in Table 1. These data specify the membranes used in the present studies. The feed flow conditions used in all the experiments carried out in the present studies are specified in terms of the corresponding values of the mass transfer coefficient, k, obtained with the reference sodium chloride solution system containing 1500 mg/l salt. In order to evaluate the relative performance of the membranes for feed solutions 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 in terms of easily obtainable parameters for a convenient and well-studied reference feed solution system such as an aqueous sodium chloride solution. The data presented in Table 1 show

TABLE 1

Membrane Specification Data[a]

Film no.	$A \times 10^6$ g-mole H_2O ($cm^{-2}sec^{-1}atm^{-1}$)	D_{AM}/K_δ for NaCl (10^5 cm/sec)	Feed concentration, 1500 mg/l NaCl; $k = 10.24 \times 10^{-4}$ cm/sec: Solute separation (%)	Product rate (g/hr)
1	1.63	3.23	91.56	19.52
1	1.68	2.73	91.64	20.00

[a] Film area 11.4 cm^2; pressure 300 psig.

the high productivity of the cellulose acetate membranes used in the present studies at low operating pressure (100 to 300 psig).

Calculation of Solute Transport Parameter

The experimental data on product rates (*PR*) and solute separation were used in the calculation of solute transport parameter values from

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

where *s* is the effective membrane area, *d* is the density of the solution, and *k* is the mass transfer coefficient. The values of the mass transfer coefficient, *k*, were calculated using

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

where k_{ref} is the mass transfer coefficient for the reference system of 1500 ppm of aqueous sodium chloride solution (10.24×10^{-4} cm/sec) and $(D_{AB})_{\text{ref}}$ and D_{AB} refer to the diffusivity of sodium chloride and the nickel salt, respectively.

The diffusivity values of the nickel salts used in the studies were calculated using the Nernst equation:

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

where z_+ and z_- represent the valencies of the cation and the 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.

The calculated values of the diffusivity and the mass transfer coefficients for the nickel salts are presented in Table 2. The data on the solute transport parameter, D_{AM}/K_δ together with solute separation and product rate are given in Table 3.

Separation of Different Nickel Salts

The effect of pressure (100 to 300 psig) on the degree of solute separation and the product rates for nickel nitrate, nickel chloride, and nickel sulfate solutions containing 1000 ppm of nickel are illustrated in Fig. 1.

TABLE 2

List of Solutes Used with Some Physicochemical Data

No.	Solute	λ_+^0	λ_-^0	$D_{AB} \times 10^5$ (cm^2/sec)	$k \times 10^4$ (cm/sec)
1	$Ni(NO_3)_2$	50.5	71.42	1.1809	8.328
2	$NiCl_2$	50.5	76.44	1.214	8.483
3	$NiSO_4$	50.5	80.80	0.8270	6.567

TABLE 3

Data on Solute Transport Parameters[a]

Salt	Solute separation	Product rate (g/hr)	k (cm/sec)	$D_{AM}/K\delta$ (cm/sec)
$Ni(NO_3)_2$	0.9714	18.22	8.328×10^{-4}	1.034×10^{-5}
$NiCl_2$	0.9840	18.52	8.483×10^{-4}	0.5805×10^{-5}
$NiSO_4$	0.9920	19.55	6.567×10^{-4}	0.3038×10^{-5}

[a] Membrane area 11.4 cm^2; pressure 300 psig.

The product rates in the case of nickel nitrate and nickel chloride for 1000 ppm of nickel feed solutions were identical, while the observed product rates for nickel sulfate solution were slighly higher. The solute separation and product rate as a function of pressure (100 to 300 psig) were also determined for feed solutions containing 500 and 100 ppm nickel. The product rates were identical for all the three nickel salts in the case of nickel feed solutions containing 500 and 100 ppm of nickel. In general, the product rates increased linearly with operating pressures and decreased slightly with an increase in feed concentrations; these experimental observations are similar to those reported for many other solution systems *(11)*. It is clear from Fig. 1 that the solute separation levels off at a pressure of approximately 300 psig.

At a given operating pressure, the separation of nickel nitrate is less than nickel chloride, which in turn is less than nickel sulfate. This trend in the separation behavior holds good at all the feed concentrations used in the present studies (100, 500, and 1000 ppm Ni). The observed order of solute separation of the nickel salts [$NiSO_4 > NiCl_2 > Ni(NO_3)_2$] can be attributed to the concentration of ion-paired species present in the solutions.

Solute separation data (300 psig) for $Ni(NO_3)_2$, $NiCl_2$, and $NiSO_4$ are plotted in Fig. 2 as a function of log K, where K is the equilibrium

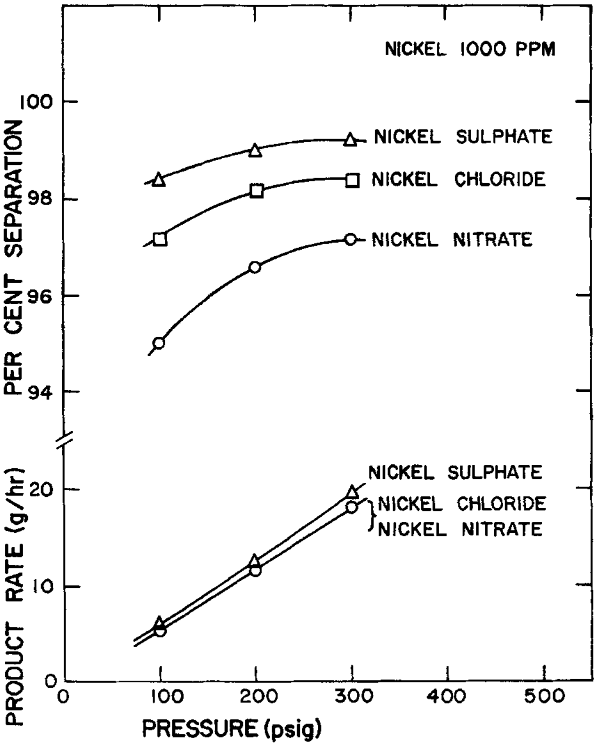

FIG. 1. Separation of nickel salts (=1000 ppm) as a function of pressure.

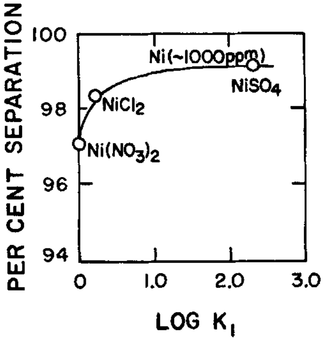

FIG. 2. Separation of nickel as a function of ion-pair equilibrium constant at 300 psig.

constant for the formation of the solvent separated ion-pair species:

$$Ni^{2+} + A^{-y} \rightleftarrows Ni^{2+}A^{-y}$$

It is clear from Fig. 2 that the percent solute separation increases with increasing values of the ion-pair equilibrium constant. Thus it is apparent that the chemical species present in solution is of importance in the reverse osmosis separation of metal ions from aqueous solutions. Earlier studies (*3*) have shown that a membrane which gave a separation of 51% with NaCl resulted in separations of 74.7, 80.3, and 95% in the cases of $Ni(NO_3)_2$, $NiCl_2$, and $NiSO_4$, respectively. Similar results were obtained in the case of zinc salt solutions (*5*). It is useful to point out in this regard that reverse osmosis treatment of a solution containing several anions like $SO_4{}^{2-}$, Cl^-, $NO_3{}^-$, and a metal ion like Ni^{2+} would result in a separation in keeping with the concentrations of ion-pairs and bare aquo metal ions. To verify this concept, the reverse osmosis separation of a mixture of nickel chloride (220 ppm) and nickel sulfate (780 ppm) was studied as a function of applied pressure and the results are depicted

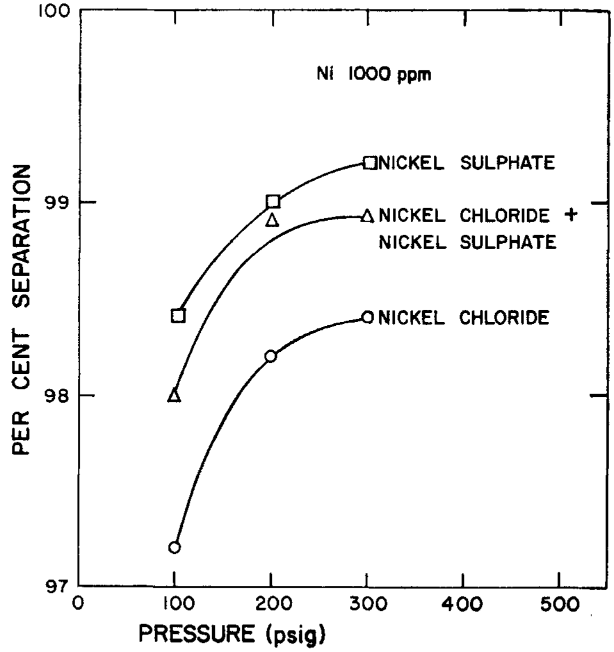

FIG. 3. Separation of nickel as a function of pressure.

in Fig. 3 along with the results obtained for nickel chloride and nickel sulfate. It is clear from Fig. 3 that the separation behavior of nickel in the mixture of nickel chloride and nickel sulfate lies between the curves represented by nickel chloride and nickel sulfate and is closer to the nickel sulfate. For example, the calculated value for the percent separation of nickel in the case of a nickel chloride–nickel sulfate mixture at a pressure of 300 psig is 99.0 which is in reasonable agreement with the experimentally observed value of 99.4.

In order to establish the effect of ion-pair species on the solute separation by reverse osmosis, experiments on the separation of nickel nitrate and nickel chloride (1000 ppm Ni) in the presence of added sodium sulfate were carried out and the resulting experimental data are shown in Fig. 4. The addition of 250 ppm of sodium sulfate to nickel nitrate solution con-

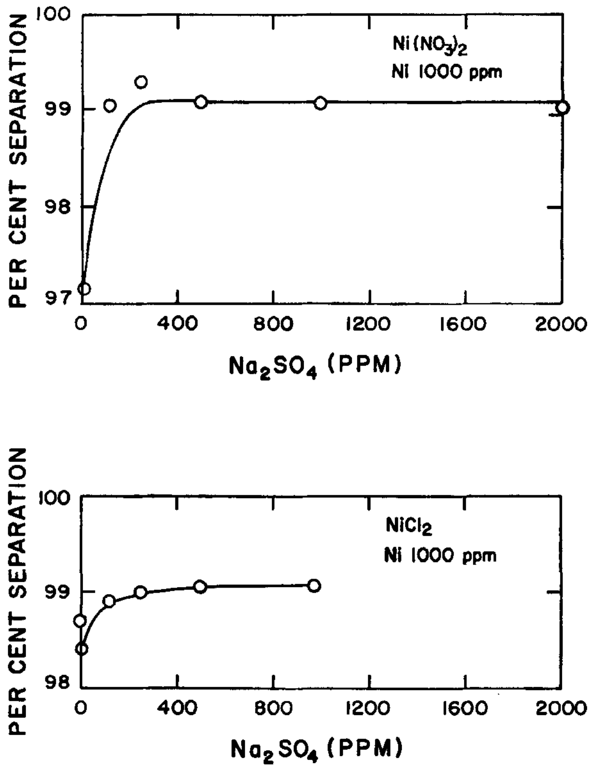

FIG. 4. Effect of Na_2SO_4 on the separation of nickel at 300 psig.

taining 1000 ppm nickel increased the solute separation from 97.2 to 99.14 (Fig. 4). The observed increase in solute separation of nickel in the presence of added sodium sulfate can be attributed to the formation of ion-pairs in solution ($Ni^{2+}SO_4^{2-}$) which are separated better than divalent aquo nickel ions. Similar observations have been made in the case of zinc salt solutions (*5*). These results are significant in some practical situations. In the case of solutions containing metal nitrate or metal chloride, it is possible to increase the separation of the metal ion in question by the addition of sodium sulfate and at the same time obtain high product water recovery by using more porous cellulose acetate membranes. Thus these results can be considered as significant for practical industrial treatment of barren metallurgical effluents containing trace amounts of metal ions associated with nitrate or chloride anion.

Effect of Organic Brighteners on Membrane Performance

Industrial nickel-plating solutions usually contain some organic brightener agents (*12*). Hence the effect of organic brighteners on the performance of the membranes is of practical interest from the point of view of the reverse osmosis treatment of industrial nickel-plating wastewater. The effect of the Canadian Hanson nickel brighteners No. 61 and 63 on the reverse osmosis performance of the membranes in the treatment of nickel solutions of the composition:

$NiSO_4$	780 ppm Ni
$NiCl_2$	220 ppm Ni
Boric acid	120 ppm
Brightener 61	1.1 % by volume
Brightener 63	2.1 % by volume

was investigated. The total volume of the brighteners of 3.2 % by volume was taken as unit volume, and the solute separation and product rates as a function of the relative volume of the organic brighteners (0 to 4.0) were determined. The results are depicted in Fig. 5. The separation of nickel was essentially constant. The product rates decreased from 17.08 to 8.08 g/hr, corresponding to the relative volume of organic brightener of 0.5 and 4.0, respectively. The decrease in product rate can be attributed to the increase in viscosity of the feed solution upon addition of the organic brighteners.

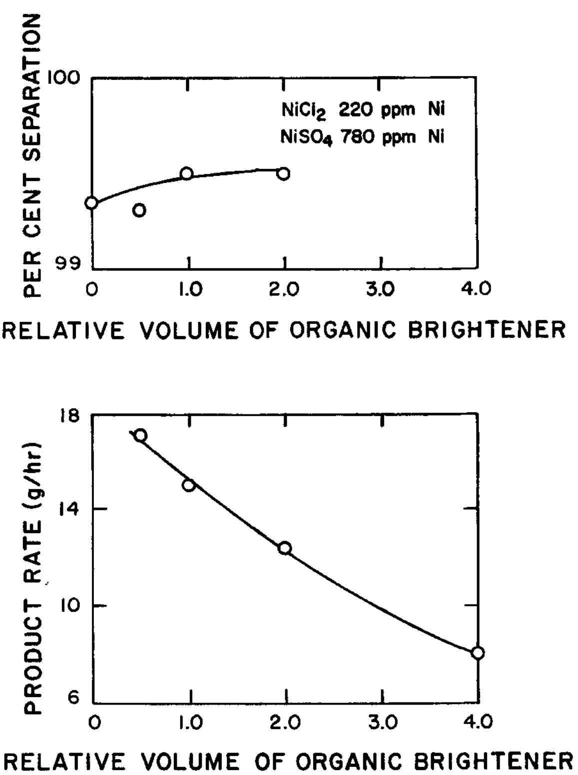

FIG. 5. Effect of organic brighteners on the separation of nickel and product rate.

Effect of Nickel Concentration in the Feed on Membrane Performance

The effect of varying the concentration of nickel sulfate on the reverse osmosis characteristics such as percent solute separation and product rate (flux rate) was studied. The results on the product rate and percent solute separation for the feed concentration range of 1,000 to 10,000 ppm of nickel sulfate are given in Table 4. These results were obtained using the static cell which gave a mass transfer coefficient (*k*) value of 10.24×10^{-4} cm/sec for the reference system of 1500 ppm of aqueous sodium chloride solution. Because divalent salts, such as nickel sulfate, are separated better than monovalent salts, such as sodium chloride, the average pore size on the membrane surface required to yield a given level

TABLE 4

Separation of Nickel Sulfate[a]

$NiSO_4$ (ppm)	Pressure (psig)	Product rate (g/hr)	Separation (%)
1,140	300	14.83	96.32
4,470	300	12.22	97.32
8,940	300	9.50	97.20
13,800	300	7.22	97.10

[a] Membrane area 11.4 cm^2.

of solute separation is higher for nickel salts than that needed for sodium chloride. From the data given in Table 4 it is clear that the solute separation remains essentially constant while the product rate decreases from 14.8 to 9.5 g/hr in going from 1000 to 9000 ppm of nickel in the feed solution. From the point of view of obtaining product water for recycle operations, the cellulose acetate membranes used in the present work are adequate in that a product rate of 9.5 g/hr at a concentration of 9000 ppm of nickel and solute separation of 97.2% can be obtained. Thus cellulose acetate membranes giving 91.6% separation of sodium chloride are adequate for producing product water of suitable quality for recycle operations.

The results obtained in this study are useful in predicting the general reverse osmosis behavior of metals such as Mg, Mn, Zn, Cu, and Pb present in acid mine-water (New Brunswick, Canada). For example, it can be predicted that the separation of metal salts will be in the order $MSO_4 > MCl_2 > M(NO_3)_2$, where "M" refers to Mg, Mn, Zn, and Cu.

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