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 Bhattacharyya, D. , Shelton, S. and Grieves, R. B.(1979) 'Charged Membrane Ultrafiltration of Multisalt Systems: Application to Acid Mine Waters', Separation Science and Technology, 14: 3, 193 — 208

To link to this Article: DOI: 10.1080/01496397908066958

URL: http://dx.doi.org/10.1080/01496397908066958

SEPARATION SCIENCE AND TECHNOLOGY, 14(3), pp. 193–208, 1979

Charged Membrane Ultrafiltration of Multisalt Systems: Application to Acid Mine Waters

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Abstract

Ultrafiltration of dissolved and precipitated inorganic salts from synthetic and actual acid mine waters is investigated experimentally in a bench-scale, continuous-flow unit, utilizing negatively charged, noncellulosic membranes. The process is evaluated in terms of the simultaneous achievement of good water flux without membrane fouling and of adequate ultrafiltrate quality at high water recovery for water reuse operation. At a transmembrane pressure of 5.6×10^5 N/m^2 and a channel Reynolds number of 6,000, the flux drop is less than 30%, even with a concentrated acid mine water containing 16,000 mg/l total solids and a high $CaSO_4$ concentration. At 90% ultrafiltrate recovery, depending on the type of noncellulosic membrane utilized, 98% iron removal, 85% aluminum removal, and 50 to 73% calcium and manganese removals can be obtained at an average water flux from 6.4×10^{-4} to 13.2×10^{-4} cm/sec. The overall ultrafiltrate quality is considerably better than that observed with a lime precipitation process.

INTRODUCTION

Acid mine water is a problem of critical significance in most coal-producing regions. The construction of coal conversion plants will produce a greatly increased demand for both coal and water and will provide a great impetus for the recycle and reuse of treated acid mine drainage water. Acid mine water is produced by oxidation and hydrolysis of pyrite (FeS_2) exposed during coal mining. The resulting acid water, containing

H_2SO_4, Fe^{2+}, and Fe^{3+}, dissolves various metals (Ca, Mg, Al, Mn, etc.) from the surrounding strata and produces highly contaminated water containing $SO_4{}^{2-}$, H^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, and other heavy metal ions.

Charged membrane ultrafiltration provides a unique and broadly applicable technique for the simultaneous separation of various inorganic metal ions (including precipitates) present in industrial wastewaters. Negatively charged, anisotropic, noncellulosic membranes (10×10^{-8} to 20×10^{-8} cm pore widths) provide high water flux and adequate rejections of metals (and sulfate) at low transmembrane pressures (5×10^5 to 7×10^5 N/m^2). This process is particularly appropriate for applications requiring water reuse in which completely demineralized water is not warranted. Bhattacharyya et al. have demonstrated promising ultrafiltration results with electroplating rinse waters (*1*), waters of high hardness (*2*), complex wastewaters containing organic and inorganic solutes (*3*), and nonferrous metal production wastewaters containing high concentrations of heavy metals (*4*). Sachs (*5*) and Mizrahi et al. (*6*) have used charged membranes with primary and secondary sewage effluents and obtained good water flux at low pressures.

The separation of ionic solutes by charged ultrafiltration membranes is due to repulsion of coions by the fixed charged groups in the membrane skin. The attainment of adequate separation at low pressure without membrane compaction problems and the nonfouling nature with solutions containing high concentrations of suspended solids are attractive features of charged membranes. These membranes are primarily suitable for dilute to moderately concentrated solutions of low effective osmotic pressures. Reverse osmosis membranes (operated at pressures above 3×10^6 N/m^2), in contrast, are used for water desalination and/or for wastewaters of high osmotic pressures for which very high rejections (98.0 to 99.9%) of all inorganic ions are desired.

The treatment of acid mine waters by charged membrane ultrafiltration for the purpose of water reuse is a very promising application. Most physicochemical treatment methods reported in the literature are primarily directed toward removal of acidity and iron (the lime neutralization process) or for the production of a very high quality water (the reverse osmosis process). The lime (or limestone) neutralization process (*7*, *8*) produces water containing high dissolved solids, saturated calcium sulfate (leading to scale formation problems), and colloidal hydroxide precipitates, and the treated water is not suitable for industrial reuse.

The high-pressure reverse osmosis process (*9*, *10*) produces a high quality demineralized water, but the water flux drop due to the calcium sulfate fouling problem limits water recovery.

A treatment plant concept utilizing charged membrane ultrafiltration to convert acid mine drainage water (after the necessary pH adjustment) for reuse in mine-mouth coal conversion facilities is shown in Fig. 1. High ultrafiltrate water recovery (90 to 95% of the feed flow) and adequate ultrafiltrate water quality are essential for the reuse scheme. The blowdown rate requirement is dependent on the ultrafiltrate quality and on the water consumption in the coal conversion process. The overall objective of this investigation is the experimental evaluation and development of the ultrafiltration unit to treat acid mine waters (over a broad concentration range), providing a degree of treatment sufficient for water reuse and for the concommitant elimination of some of the problems inherent to the reverse osmosis and/or lime neutralization processes. The water flux behavior and separation characteristics are experimentally investigated in a bench-scale, continuous flow ultrafiltration unit, utilizing commercially available, negatively charged ultrafiltration membranes.

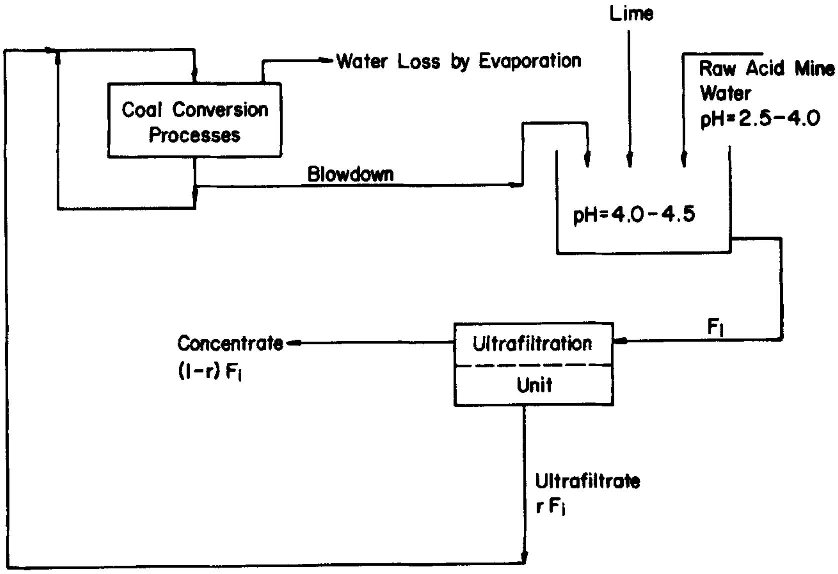

FIG. 1. Schematic of acid mine water treatment process for ultrafiltrate reuse.

EXPERIMENTAL

The continuous-flow, steady-state (6 to 8 hr operation) experiments at 25 ± 1 °C were conducted in a thin-channel (0.08 cm height, 1.3 cm width) unit containing 50.3 cm^2 of commercially available charged ultrafiltration membrane. Figure 2 shows the experimental unit used in the study. Channel velocity was varied in the range of 40 to 430 cm/sec at a constant transmembrane pressure of 5.6×10^5 N/m^2. The feed composition was maintained constant by the recycle of both the concentrate and the ultrafiltrate streams to the feed tank.

Two types of noncellulosic membranes (Millipore PSAL and Millipore PTAL) containing negatively charged, sulfonic acid functional groups were used. Millipore PSAL (noncellulosic skin on cellulosic backing) membranes have a pH tolerance limit of 2.5 to 11 and a maximum temperature limit of 35°C. Millipore PTAL membranes (noncellulosic skin and backing) have a broader pH tolerance limit (pH 1 to 12) and a higher (70°C) temperature limit. During the initial phase of the study, several tailored PSAL and PTAL membranes of different water flux characteristics were evaluated.

The synthetic (1 ×) and actual acid mine waters used in this study are shown in Table 1. The synthetic waste was prepared with Reagent Grade metal sulfate salts, and the acidity was adjusted with H_2SO_4. In order to simulate high water recovery and possible membrane fouling

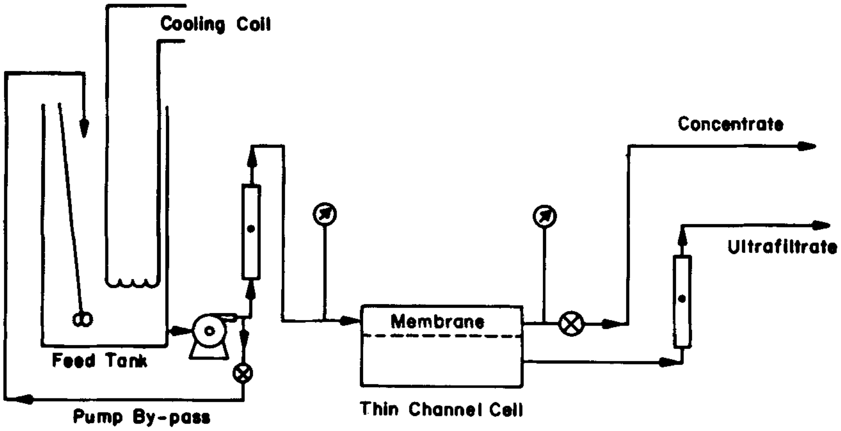

FIG. 2. Schematic diagram of experimental ultrafiltration unit.

TABLE 1

Composition of Acid Mine Waters

Component	Synthetic (1 ×)	Actual[a]
pH	2.5	3.1
Conductivity	3020 μmho/cm	1050 μmho/cm
Acidity	570 mg/l	320 mg/l
Total solids	2050	650
Suspended solids	75	150
Ca^{2+}	200	50
Fe^{3+}	100	35
Al^{3+}	30	5
Mg^{2+}	30	—
Mn^{2+}	10	2.5
$SO_4{}^{2-}$	1350	280

[a] Western Kentucky.

problems, experiments were also conducted with 5 × and 10 × synthetic wastes. All pH adjustments (prior to ultrafiltration) were made with lime slurry.

Analyses were performed on the steady-state feed streams and the steady-state ultrafiltrate streams to determine the separation achieved. The metals Ca, Fe, Al, and Mn were analyzed by atomic absorption. In addition to the metals, total solids, total suspended solids, and conductivity were also monitored.

RESULTS AND DISCUSSION

Membrane processes are generally evaluated in terms of two parameters: membrane rejection (R) and water flux (J_w). The membrane rejection parameter, R, is a measure of the extent of the separation:

$$R = 1 - \frac{C_f}{C_i} \tag{1}$$

in which C_f is the metal concentration in the ultrafiltrate stream and C_i is the concentration of the same metal ion in the feed stream. With charged membranes, rejection generally decreases with an increase in feed concentration (*1*, *2*). The water flux parameter, J_w, is a measure of the water transport (ultrafiltrate flow rate per unit membrane area) through the membrane; for feed streams containing dissolved ions and suspended solids, J_w is related to transmembrane pressure, Δp, by

$$J_w = \frac{\Delta p - \Delta\Pi}{R_m + R_f} \tag{2}$$

in which $\Delta\Pi$ is the osmotic pressure difference, R_m is the membrane resistance for solute-free water, and R_f is the resistance due to the formation of a suspended solids layer on the membrane surface (*3*). The osmotic pressures of acid mine waters are quite low and generally less than 0.5×10^5 N/m^2.

For an ultrafiltration process to be feasible for the treatment of acid

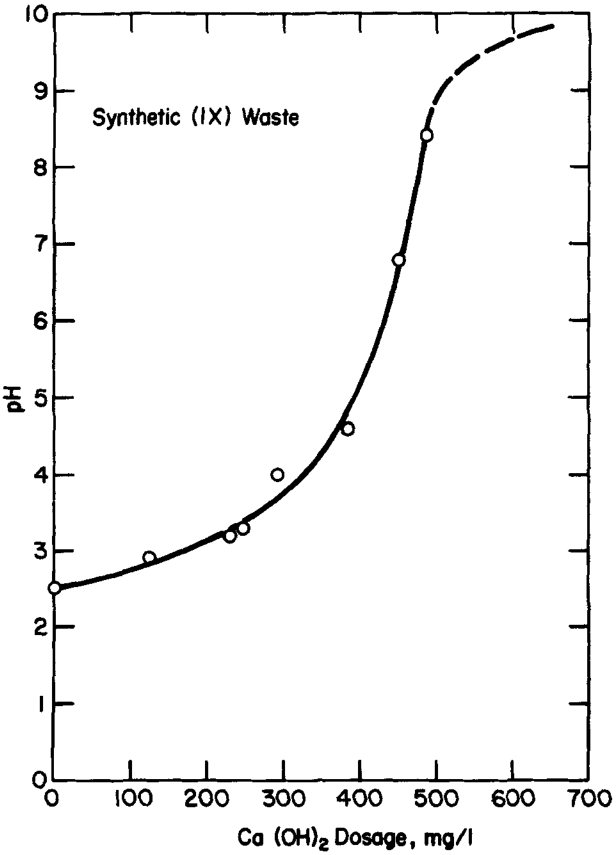

FIG. 3. Determination of lime dosage as a function of pH.

mine waters, the membranes must be capable of totally rejecting suspended solids and adequately rejecting dissolved solids (metals, sulfate), and, in particular, a substantial membrane water flux loss must be avoided. Preliminary studies were conducted with several tailored, charged membranes of different "initial" water flux (membrane resistance) values. Because the feed stream pH, calcium sulfate content, and suspended solids content would be expected to affect membrane performance, the lime dosage requirement for the synthetic 1 × waste was first established (Fig. 3). The suspended solids (iron and aluminum hydroxide) increased considerably above pH 5, and therefore all preliminary membrane evaluations were conducted below pH 4.5. The overall rejection (in terms of total solids) behavior and flux characteristics with synthetic and actual wastes are shown in Figs. 4 and 5 as a function of the "initial" water flux (solute-free water). The initial water flux corresponds to $\Delta\Pi$ and R_f equal to zero in Eq. (2). Although all membranes rejected 100% of the suspended solids, the total solids (suspended solids plus dissolved solids) rejection dropped sharply for membranes with an initial water flux greater than 25×10^{-4} cm/sec (membrane resistance $R_m < 2.2 \times 10^8$ N/m^2/cm/sec). Membranes of initial water flux less than 25×10^{-4}

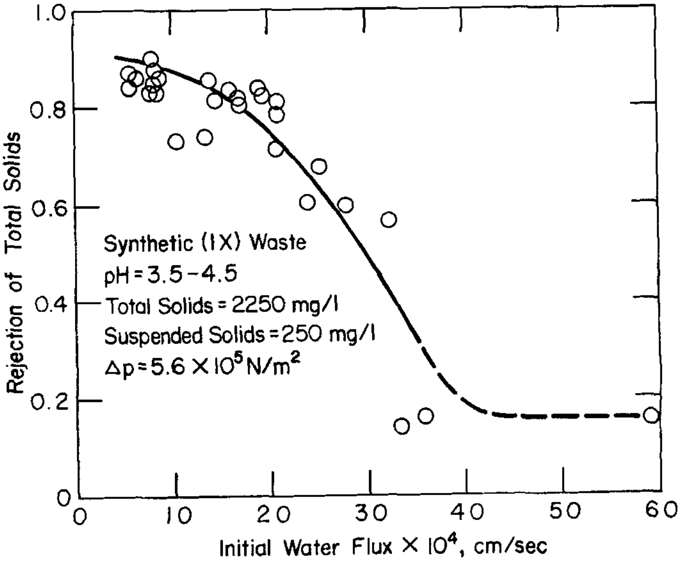

Fig. 4. Dependence of total solids rejection on initial membrane water flux.

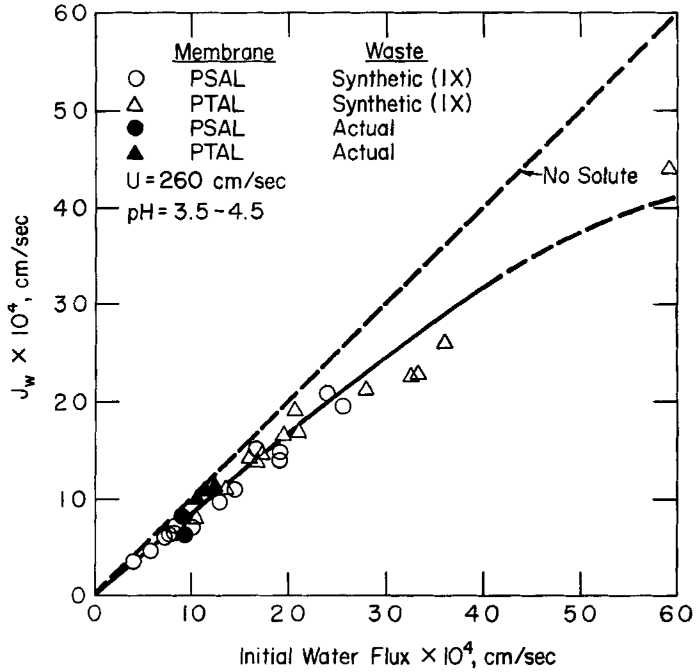

FIG. 5. Dependence of steady-state water flux on initial membrane water flux.

cm/sec (at $\Delta p = 5.6 \times 10^5$ N/m^2) provided a flux drop of only 10 to 15%. Therefore, one specific PSAL membrane (initial water flux = 8.2×10^{-4} cm/sec at $\Delta p = 5.6 \times 10^5$ N/m^2) and one specific PTAL membrane (initial water flux = 17.3×10^{-4} cm/sec at $\Delta p = 5.6 \times 10^5$ N/m^2) were then extensively evaluated with acid mine waters. These specific PSAL and PTAL membranes had pore widths of approximately 12×10^{-8} and 18×10^{-8} cm, respectively.

The effects of channel velocity U on the lower (PSAL) and higher (PTAL) flux membranes are shown in Fig. 6. Membrane fouling was observed below a channel velocity of 80 cm/sec. Above a U of 250 cm/sec (Reynolds number = 7500), the flux gain was insignificant. At $U = 200$ cm/sec, flux drops of 9 and 13% were observed with the PSAL and PTAL membranes, respectively. To simulate high water recovery, concentrated (synthetic) acid mine waters with high total solids were also ultrafiltered; both membranes showed a drop of only 28% at the high concentrations, as shown in Fig. 7. Even with a 10× waste containing 16,000 mg/l total

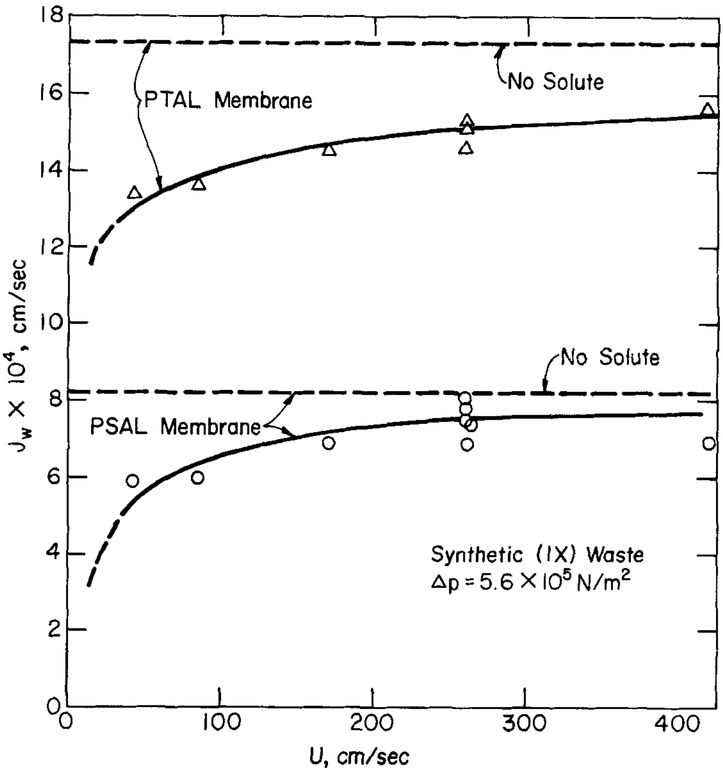

FIG. 6. Effect of average channel velocity on steady-state water flux.

solids (including a high $CaSO_4$ concentration), the water flux was maintained at 12.5×10^{-4} cm/sec with the PTAL and 5.8×10^{-4} cm/sec with the PSAL. Excellent flux stability was also observed over a long time period (56 hr) with a 1 × waste and the provision of only tap water flushing.

The membrane rejection behavior (with synthetic 1 × wastes) of the various metals is shown in Fig. 8 for the PSAL membrane. At pH 3.0 no metal hydroxide precipitates were present, and Fig. 8 shows excellent soluble metal rejections. At pH 4.0, 50% of the Fe and 30% of the Al shown in Table 1 were present as precipitates, and thus the simultaneous removals of dissolved metal ions and precipitated metals were obtained. At pH 5.0, extensive (99%) Fe precipitation occurred, and therefore the optimum ultrafiltration pH should be around 4.0. With the PTAL mem-

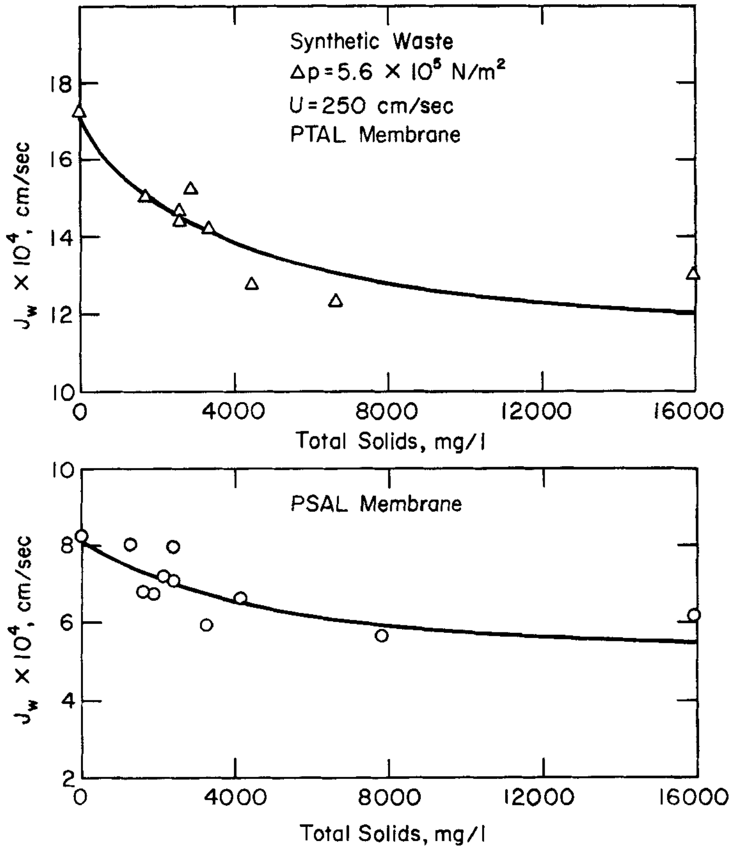

FIG. 7. Dependence of steady-state water flux on feed stream total solids concentration.

brane, Fe^{3+} and Al^{3+} rejections were similar to those with PSAL, whereas Mn^{2+} and Ca^{2+} rejections were somewhat lower (0.78 for Mn and 0.79 for Ca). The membrane rejections obtained with the actual acid mine water (pH adjusted to 4.0) were similar to those obtained with the synthetic waters and the results are shown in Table 2. Good metal rejections were again observed, even with the high flux PTAL membrane.

With charged membranes, because the ultrafiltrate concentration generally increases ($C_f = KC_i^n$ or $R = 1 - KC_i^{n-1}$) with an increase in the feed concentration (*1*, *2*, *4*), a series of experiments was also con-

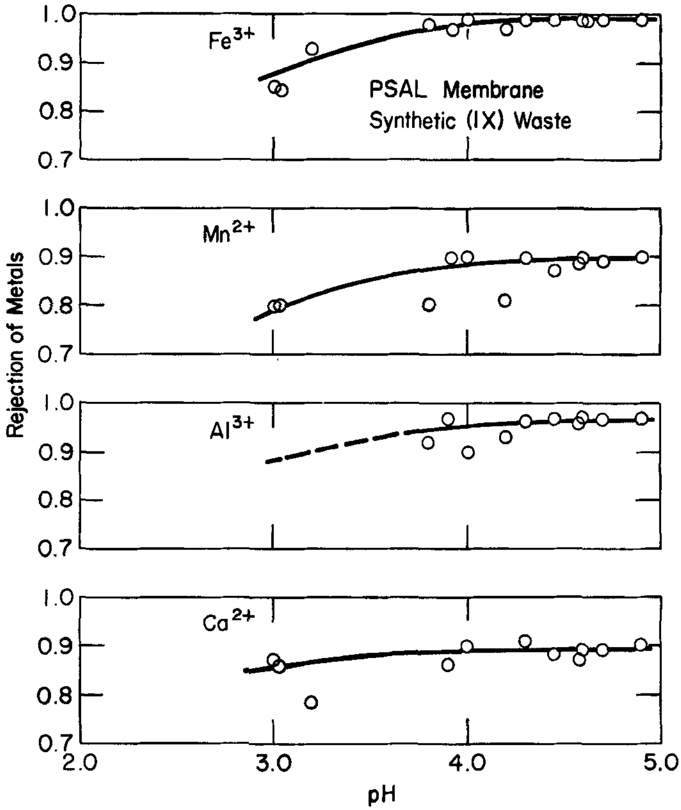

FIG. 8. Effect of pH on rejections of metals.

TABLE 2

Metal Rejections Obtained with Actual Acid Mine Water: pH = 4.0, $\Delta p = 5.6 \times 10^5$ N/m^2

	PSAL membrane[a]	PTAL membrane[b]
Fe	0.97	0.95
Al	0.95	0.93
Mn	0.89	0.85
Ca	0.83	0.79
Suspended solids	1.0	1.0

[a] Water flux with waste: 7.8×10^{-4} cm/sec.

[b] Water flux with waste: 15.9×10^{-4} cm/sec.

ducted over a tenfold (up to 10 ×) concentration range in order to simulate the effects of high water recovery. Over the entire concentration range, the rejections (with both membranes) of Ca and Fe remained constant ($n = 0$) and the rejections of Al and Mn decreased somewhat ($n = 1.2$) with concentration. Although the sulfate concentrations in the ultrafiltrate streams were not monitored, sulfate rejection would have to parallel the metal rejections because sulfate was the principal anion present in the wastes.

SCALE-UP CONSIDERATIONS

For full-scale (Fig. 1) operation of an ultrafiltration unit, high water (ultrafiltrate) recovery is essential for water reuse and to reduce the concentrate volume from the membrane unit. At high water recovery (90% or more), an adequate degree of soluble metal (including Ca) and sulfate (to maintain $CaSO_4$ below saturation) separation and complete removal of suspended solids must be achieved without a significant water flux loss. Water recovery, r, can be increased by multiple ultrafiltration module units involving an optimum tapered arrangement (*1*, *3*, *4*). Utilizing a simulation technique developed by Bhattacharyya et al. (*1*, *11*), the effects of water recovery on solute removal for various membrane rejection values were calculated and the results are shown in Fig. 9 for two general cases. The solute removal shown on the ordinate is based on the average ultrafiltrate concentration from all of the membrane modules in the full-

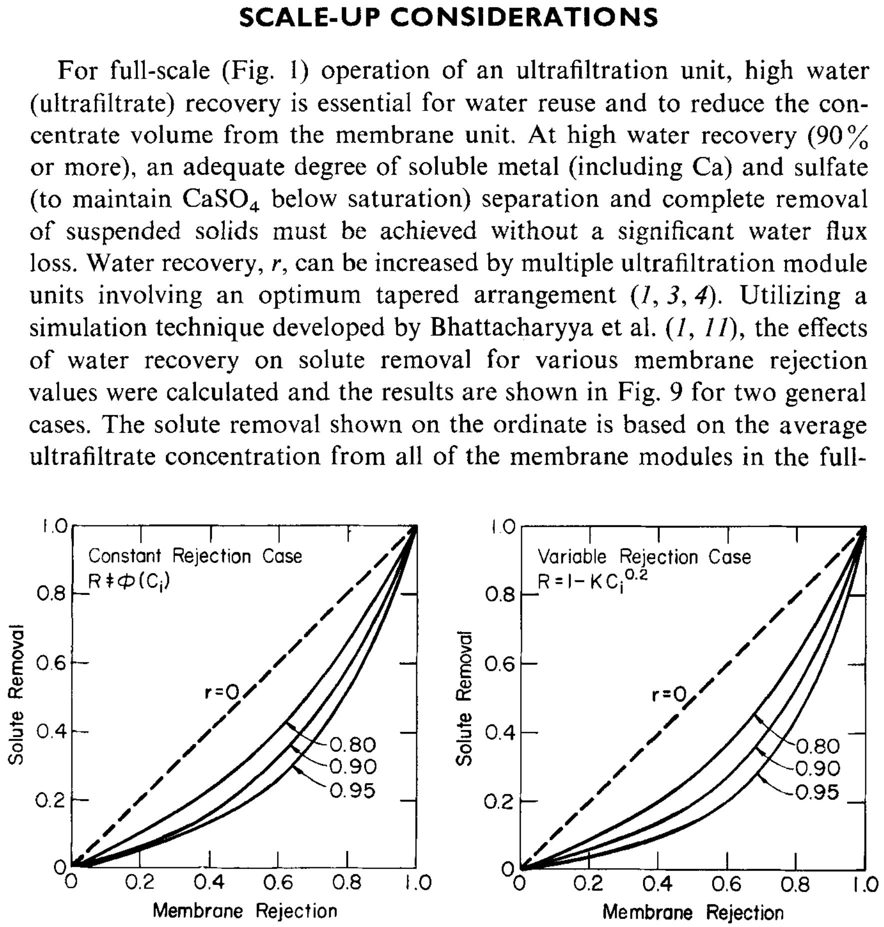

FIG. 9. Prediction of solute removals as a function of membrane rejection for specified water recoveries.

scale unit and is equal to $1 - C_{f\ \text{average}}/C_i$. The membrane rejection, R, shown on the abscissa is the rejection obtained in a laboratory-scale unit involving no water recovery, such as those shown in Fig. 8 and Table 2. For example, Fig. 9 shows that with a metal rejection of 0.9 (at $r = 0$), 90% water recovery ($r = 0.9$) would decrease the overall solute removal to 0.77 for the constant rejection case ($R \neq \phi(C_i)$) and to 0.72 for the variable rejection case ($R = 1 - KC_i^{0.2}$).

Using the laboratory rejection values obtained with the 1× acid mine water (at pH 4.0) together with Fig. 9, the removals of the metals at 90% ($r = 0.9$) water recovery were calculated and are shown in Table 3 for both the PSAL and PTAL membranes. The Fe and Al removals were quite excellent with both membranes, but the Ca and Mn removals were considerably lower with the high flux PTAL membrane. For the acid mine water (1× waste) shown in Table 1 (with a total Ca of 380 mg/l due to added lime), even with the PTAL membrane the molar concentration of $[Ca^{2+}][SO_4^{2-}]$ in the ultrafiltrate would be only 1/16 of the saturation concentration (solubility product of $CaSO_4 = 2.2 \times 10^{-4}$). The ultrafiltrate quality can be compared with the quality of the supernatant obtained by lime precipitation-settling at pH 8 of the 1× waste. The supernatant from the lime precipitation process contained 457 mg/l Ca^{2+}, 1350 mg/l SO_4^{2-}, 3.1 mg/l Fe^{3+}, 3.3 mg/l Mn^{2+}, and 85 mg/l suspended solids; the molar $[Ca^{2+}][SO_4^{2-}]$ concentration was close (Ca^{2+} and SO_4^{2-} removals were zero) to the saturation point, and thus water reuse could not be practiced with the pH 8 lime precipitation process.

The concentrate stream flow from the ultrafiltration unit would be 10% of the feed stream flow, with operation to achieve 90% water re-

TABLE 3

Removal of Metals at 90% Water Recovery: pH = 4.0, $\Delta p = 5.6 \times 10^5$ N/m^2

	PSAL membrane[a]	PTAL membrane[b]
Fe	0.98	0.98
Al	0.85	0.84
Mn	0.70	0.50
Ca	0.73	0.59
SO_4	0.83	0.74
Suspended solids	1.0	1.0

[a] Average water flux: 6.4×10^{-4} cm/sec.

[b] Average water flux: 13.2×10^{-4} cm/sec.

covery. The concentrate flow rate could be decreased further by post-settling prior to additional processing by the membrane unit (*10*).

The major operating costs for the ultrafiltration unit would be the sum of the membrane replacement cost (2-year membrane life) plus the pumping cost to overcome frictional pressure losses. The membrane area requirement would be dependent on the ultrafiltrate quality requirement necessary for water reuse and on the water recovery. For an acid mine water flow rate of 3.8×10^6 l/day, 90% water recovery could be achieved with 3.0×10^3 m^2 of PTAL (with ultrafiltrate quality lower than PSAL) or 6.2×10^3 m^2 of PSAL membrane.

CONCLUSIONS

Low-pressure ultrafiltration with negatively charged, noncellulosic membranes is shown to be a feasible process in terms of achieving the simultaneous separation of dissolved metals (and sulfate) and of suspended solids from acid mine drainage water. The process is evaluated in terms of the simultaneous achievement of good water flux without membrane fouling and of adequate ultrafiltrate quality at high water recovery for water reuse operation.

Among the various commercially available, charged ultrafiltration membranes that were evaluated in a continuous-flow unit, membranes of initial water flux (at a pressure of 5.6×10^5 N/m^2) 8.2×10^{-4} to 17.3×10^{-4} cm/sec were found to be best suited for the treatment of acid mine waters. At the optimum operating pH of 4.0, a channel velocity of 200 cm/sec (Reynolds number = 6,000) was sufficient to minimize membrane fouling. Even with a concentrated acid mine water (10× waste) containing 16,000 mg/l total solids (including a high $CaSO_4$ concentration), the flux drop was less than 30%. With the high-pressure reverse osmosis process reported in the literature, $CaSO_4$ fouling has caused considerable flux loss and operational problems.

For an acid mine water flow rate of 3.8×10^6 l/day, 90% water recovery could be achieved with 3.0×10^3 to 6.2×10^3 m^2 of membrane area, depending on the ultrafiltrate water quality required for water reuse and the type of membrane employed. Iron and aluminum removals (at 90% water recovery) were 98 and 85%, respectively, whereas calcium and manganese removals ranged between 50 and 73%, depending on the type of membrane selected. In all cases the ultrafiltrate contained a $CaSO_4$ concentration considerably below the saturation concentration, and the overall ultrafiltrate quality was considerably better than that observed with the lime precipitation process.

SYMBOLS

C_f	concentration of metal in ultrafiltrate stream, mg/l
$C_{f\ \text{average}}$	concentration of metal averaged over all of ultrafiltrate streams from multiple module, full-scale unit, mg/l (used to calculate solute removal)
C_i	concentration of metal in feed stream to ultrafiltration unit, mg/l
F_i	flow rate of feed stream to ultrafiltration unit, cm^3/sec
J_w	steady-state water (ultrafiltrate) flux, $\text{cm}^3/(\text{sec-cm}^2$ membrane area)
Δp	average transmembrane pressure difference, N/m^2
r	fractional water recovery (total ultrafiltrate flow rate per unit feed flow rate)
R	metal rejection (Eq. 1)
R_m	resistance of ultrafiltration membrane to water flux, N/m^2/cm/sec
R_f	resistance of suspended solids layer on membrane surface, N/m^2/cm/sec
U	average channel velocity, cm/sec
K, n	constants
$\Delta\Pi$	osmotic pressure difference, N/m^2

Acknowledgments

This study was supported in part by the Office of Water Research and Technology, Department of the Interior, under the provisions of Public Law 88–379, as Project Number B-050-KY. The authors also wish to acknowledge the technical contributions of M. Moffitt, G. Balko, and C. Bynum to this work. The cooperation of Dr. Dirk deWinter, Millipore Corp., is appreciated.

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Received by editor July 14, 1978