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Charged Membrane Ultrafiltration of Toxic Metal Oxyanions and Cations from Single- and Multisalt Aqueous Solutions

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Abstract

With application to the treatment of nonferrous metals production streams, the toxic metals As(V), Se(IV), As(III), and Cd(II) are separated from single- and multisalt aqueous solutions by continuous-flow, membrane ultrafiltration with charged, noncellulosic membranes. The single-salt aqueous solutions of As(V), Se(IV), As(III), or Cd(II) are investigated over pH 5 to 10, metal concentrations in the range 0.5 to 20.0 mM, and transmembrane pressure differences from 2.8×10^5 to 5.6×10^5 N/m², with the effects of these three independent variables established on the metal rejections. The rejections of the monovalent oxyanions H_2AsO_4^- , HSeO_3^- , and H_2AsO_3^- (with sodium as the counterion) are of the order 0.85, and those of the divalent HAsO_4^{2-} , SeO_3^{2-} (and SO_4^{2-}), and of Cd^{2+} are of the order 0.95 for 6.0 mM feed streams. Comparisons are made with the halides, NO_3^- , and ClO_4^- . The rejection behavior of multisalt solutions of H_2AsO_4^- and HSeO_3^- is not influenced by the presence of sulfate, but Cd^{2+} produces a decrease in the rejection of Se(IV). For feed streams 2.0 mM each in H_2AsO_4^- , HSeO_3^- , Cd^{2+} , and Zn^{2+} at pH 5, the presence of a high sulfate concentration does not affect the metal rejections, except at greater than 14.0 mM where the Se(IV) rejection begins to decline sharply.

INTRODUCTION

Charged, noncellulosic ultrafiltration membranes provide the concomitant advantages of moderate water flux at low transmembrane pressures of 3.0×10^5 to 6.0×10^5 N/m² and the selective separation

of specific inorganic ions from multisalt solutions. In contrast, low flux, uncharged membranes must be operated at transmembrane pressures of 4.0×10^6 to 1.0×10^7 N/m² in the reverse osmosis (hyperfiltration) process. Salt rejections are generally greater than 98%, but high effective osmotic pressures are thereby produced and the selective separation of specific ionic solutes is generally not possible. Inorganic ions may be selectively separated with charged ultrafiltration membranes on the basis of ionic charge magnitude, ionic size, and hydration characteristics. It is also possible to ultrafilter selectively, on the same basis, one species of a metal, such as H_2AsO_3^- , from another species of the same metal, such as H_3AsO_3 . Bhattacharyya and Grievess (1) have reviewed extensive experimental studies with charged ultrafiltration membranes, including the rejection characteristics for several alkaline earth and heavy metal cations and for a number of oxyanions (2, 3). Charged ultrafiltration membranes containing fixed sulfonic acid groups have also been studied by Gregor (4).

The toxic metals arsenic, selenium, and cadmium are commonly found in a variety of waste and process streams in the nonferrous metals production industry. Arsenic(III), arsenic(V), and selenium(IV), generally present as oxyanions, cannot be removed from such streams by the commonly employed hydroxide precipitation technology, and cadmium(II) can only be precipitated at pH 10.5 to 11.0. Effluent limitations guidelines for arsenic are approximately 10 mg/l (~ 0.13 mM), for selenium are 5 mg/l (0.063 mM), and for cadmium are 0.5 mg/l (0.004 mM) (5). Due to the toxicity of these metals, water quality standards may prescribe in many instances even lower limits for effluent concentrations.

The objectives of this study are (1) the experimental evaluation of charged, noncellulosic membranes to remove As(V), Se(IV), and As(III) as oxyanions from aqueous solution, as a function of solution pH and thus of the oxyanion species present, and both in the absence and presence of sulfate; (2) to remove Cd(II), as Cd^{2+} with SO_4^{2-} as the counterion, and to compare this with the ultrafiltration of other heavy metals; and (3) to remove simultaneously As(V) and Se(IV) as monovalent oxyanions and Zn(II) and Cd(II) as cations, in particular establishing the effect of high Cd(II) and sulfate concentrations on the separation of As(V) and Se(IV).

EXPERIMENTAL

The continuous-flow experiments were conducted in a thin-channel unit which had a feed channel height, width, and length of 0.079, 1.27,

and 39.6 cm, respectively, providing a total membrane area of 50.3 cm².

Commercially available, Millipore PSAL, noncellulosic, charged membranes were used in all of the experiments. Although several membranes were used, each was cut from the same manufacturing lot in order to enhance the reproducibility of the experimental results. The PSAL membranes used in these experiments had the following characteristics:

Membrane: noncellulosic skin with cellulosic backing

Fixed charge: negative

Pore width: approximately 15 Å

Membrane thickness: 150 μm

Average membrane resistance: 4.5×10^8 N/m²/cm/sec

Operating pH: 2.5 to 11.0

Temperature limit: 35°C

Maximum pressure limit: 9.0×10^5 N/m²

Water flux at 5.6×10^5 N/m²: 1.2×10^{-3} cm/sec (24 gal/ft²/day)

A typical experiment was carried out by pumping the feed solution from the feed tank into the high-pressure side of the thin-channel cell. Each run was continued until a steady-state was reached, requiring an operation time of 3 to 5 hr at transmembrane pressure differences of $\Delta p = 2.8 \times 10^5$ or 5.6×10^5 N/m² and an average channel velocity of 167 cm/sec (*Re* = 2400). At this channel velocity, no concentration polarization was observed. Solution temperature was maintained at $25 \pm 1^\circ\text{C}$. At the termination of each steady-state run, the membrane was thoroughly flushed with distilled water at high flow rate and low pressure.

Initially, each new membrane was calibrated with distilled water in order to obtain the linear relationship between the ultrafiltrate flux and the transmembrane pressure difference. The calibration was reestablished before and after each run. In addition, a run with a standard solution of CaCl₂ (6.0 mM as Ca²⁺) was made periodically to determine the rejection stability of the membrane. Calcium chloride was chosen as the standard solution because its rejection (0.40 to 0.50) was particularly sensitive to changes in the membrane characteristics; if a rejection of less than 0.35 was obtained, the membrane was replaced.

The synthetic feed solutions were prepared by dissolving Analytical Reagent Grade salts (Na₂HAsO₄·7H₂O, H₂SeO₃, NaAsO₂, 3CdSO₄·8H₂O, ZnSO₄·7H₂O, and Na₂SO₄) in distilled water (conductivity 5 μmho/cm). The feed stream concentrations were varied from 0.5 to 20.0

TABLE 1

Metal	Wavelength $\times 10^9$ (m)	Flame
Arsenic	193.7	Air-acetylene
Selenium	196.0	Nitrous oxide-acetylene
Cadmium	228.8	Air-acetylene
Zinc	213.9	Air-acetylene

mM, and, when necessary, the pH of the solution was adjusted with 6.0 M H₂SO₄ or 4.0 M NaOH.

Analyses were performed on the steady-state feed streams and the steady-state ultrafiltrate streams to determine the separation achieved. The metals cadmium and zinc (at all concentrations) and arsenic and selenium (at concentrations greater than 0.2 mM) were analyzed by atomic absorption on a Varian Techtron Model 1200 Atomic Absorption Spectrophotometer. The analytical accuracy was $\pm 2\%$. Typical detection lines and flames used are listed in Table 1. The analysis of As and Se at concentrations less than 0.2 mM was performed by flameless atomic absorption (carbon rod analysis). In all cases, conductivity measurements were also used to determine overall rejections. For single salt systems involving no pH adjustment, rejections in terms of conductivity and atomic absorption were consistently identical.

RESULTS AND DISCUSSION

Salts of As(V), Se(IV), As(III), or Cd(II)

The initial series of single-salt experiments involved oxyanions of As(V) or Se(IV) over the metal concentration range 0.5 to 20 mM, pH 5 to 9, and transmembrane pressure differences $\Delta p = 1.0 \times 10^5$ to 6.2×10^5 N/m². The pH was adjusted with NaOH or H₂SO₄, and Na⁺ was the counterion to the metal oxyanions. The separations achieved are reported in terms of the membrane rejection, R , of As(V) or Se(IV):

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

in which C_f is the metal concentration in the ultrafiltrate stream and C_i is the metal concentration in the feed stream. A rejection of 1.0 corresponds to the presence of no metal in the ultrafiltrate stream.

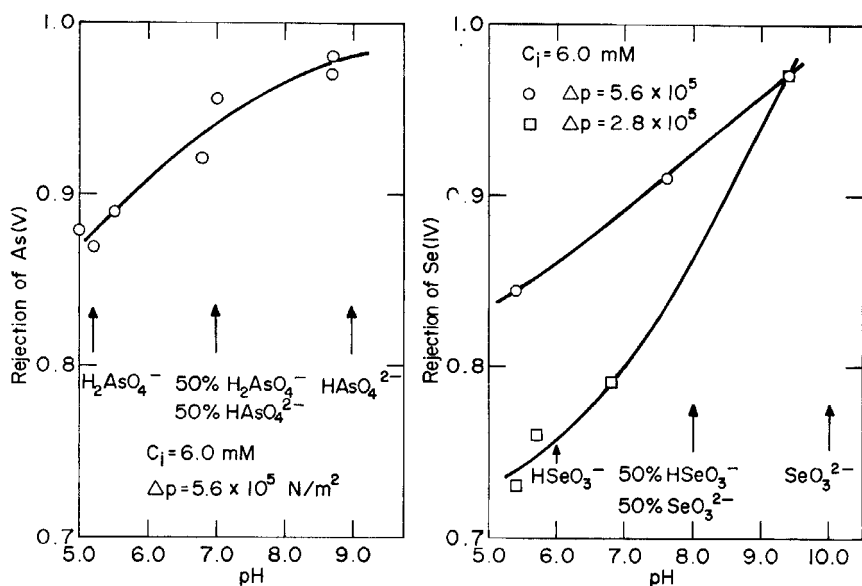


FIG. 1. Effect of pH on the rejections of As(V) and Se(IV) oxyanions from single-salt solutions.

Figure 1 indicates an increase in the rejection of As(V) as $\text{H}_2\text{AsO}_4^- \rightarrow \text{HAsO}_4^{2-} + \text{H}^+$ and in the rejection of Se(IV) as $\text{HSeO}_3^- \rightarrow \text{SeO}_3^{2-} + \text{H}^+$ as the pH was elevated from 5 to 9. The As(V) and Se(IV) oxyanion species present at various pH values are also shown in Fig. 1, with dissociation constants from Ref. 6. The effect of pH and thus of oxyanion species was more pronounced for Se(IV) at the lower transmembrane pressure difference. Higher rejections of divalent anions compared to monovalent anions have been reported previously (1, 2), and the behavior is in accord with the Donnan theory. Figure 2 indicates the influence of the transmembrane pressure difference, Δp , on the rejections of As(V) and Se(IV) at pH 5 or pH 9. The decrease in rejection at the lower Δp was due to increased diffusional transport through the membrane compared to convective transport, and the effect was greater for the monovalent oxyanions than for the divalent oxyanions. A comparison of the left and right sides of Fig. 2, both at pH 9, shows that the rejection behavior of HAsO_4^{2-} and SeO_3^{2-} was essentially the same over Δp from 2.8×10^5 to $6.0 \times 10^5 \text{ N/m}^2$.

Figure 3 presents the effect at pH 5 of C_b , the feed stream concentration,

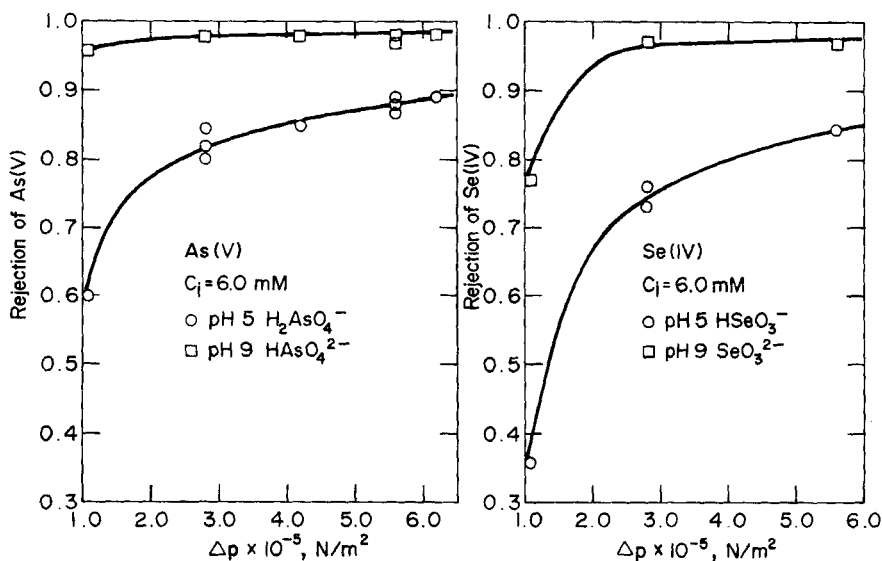


FIG. 2. Effect of transmembrane pressure difference on the rejections of As(V) and Se(IV) oxyanions at pH 5 and at pH 9 for single-salt solutions.

on C_f , the ultrafiltrate concentration (and thus on the rejection behavior) for H_2AsO_4^- and for HSeO_3^- , both at $\Delta p = 5.6 \times 10^5$ N/m². Power functions gave an excellent fit for both metals. For As(V):

$$C_f = 0.092C_i^{1.15} \quad (1)$$

or

$$R = 1 - 0.092C_i^{0.15}$$

For Se(IV):

$$C_f = 0.12C_i^{1.15} \quad (2)$$

or

$$R = 1 - 0.12C_i^{0.15}$$

The average percent deviations of values calculated with Eqs. (1) and (2) from the experimental values were 9.4% (9 points) and 7.3% (5 points) for Eqs. (1) and (2), respectively. Equations (1) and (2) show that the rejection decreased slightly with an increase in C_i . Similar relations were established at $\Delta p = 2.8 \times 10^5$ N/m² and were of the form $R = 1 -$

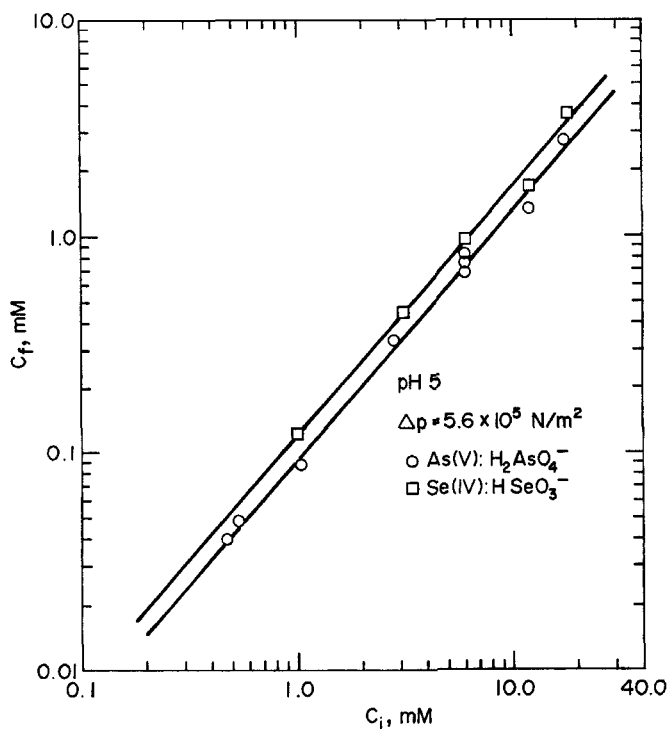


FIG. 3. Effect of feed stream metal concentration on ultrafiltrate stream metal concentration for single-salt solutions of As(V) or Se(IV) at pH 5.

$K_1 C_i^{0.25}$, indicating that the rejection was a stronger decreasing function of C_i at the lower transmembrane pressure difference. The constant K_1 at the lower Δp was, of course, greater than the corresponding values in Eq. (1) and (2). Analogous behavior was reported for the sodium salts of the monovalent oxyanions H_2PO_4^- , HCO_3^- , and HCrO_4^- at $\Delta p = 2.8 \times 10^5 \text{ N/m}^2$: $R = 1 - K_2 C_i^{0.25}$, in which K_2 was a function of the oxyanion (1, 2). For NaCl at $\Delta p = 2.8 \times 10^5 \text{ N/m}^2$, the rejection was a stronger decreasing function of C_i : $R = 1 - K_3 C_i^{0.40}$ (1, 2).

The effect at pH 9 of C_i on C_f (and thus on the rejection behavior) for HAsO_4^{2-} and for SeO_3^{2-} at $\Delta p = 2.8 \times 10^5$ and $5.6 \times 10^5 \text{ N/m}^2$ is presented in Fig. 4. Additional data from this study for Na_2SO_4 are included. The straight line was taken from data from previous investigations for the sodium salts of SO_4^{2-} , CrO_4^{2-} , and HPO_4^{2-} (1, 2):

$$C_f = 0.042C_i^{1.10}$$

or

(3)

$$R = 1 - 0.042C_i^{0.10}$$

The accuracy of Eq. (3) was only about 60% for these 19 new data points, but was reasonable considering the use of several different membranes (all Millipore PSAL) and two different operating pressures. The single relation gave a fairly good approximation for all five divalent oxyanions: HAsO_4^{2-} , SeO_3^{2-} , SO_4^{2-} , CrO_4^{2-} , and HPO_4^{2-} . Compared to monovalent oxyanions, the rejection of divalent oxyanions was a weaker decreasing function of C_i .

The next series of single-salt experiments involved the oxyacid (H_3AsO_3) and oxyanion (H_2AsO_3^-) of As(III) at a feed stream metal concentration

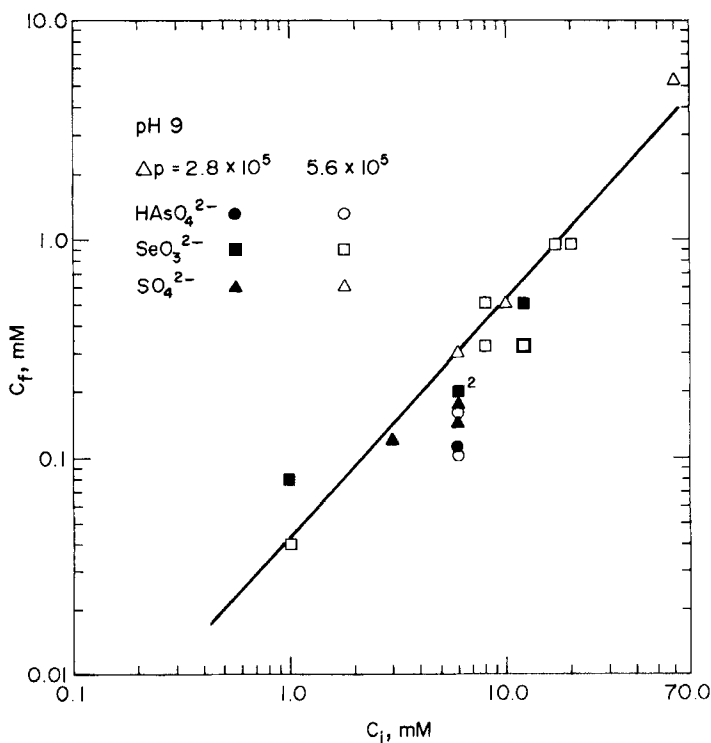


FIG. 4. Effect of feed stream metal concentration on ultrafiltrate stream metal concentration for single-salt solutions of As(V), Se(IV), or sulfate at pH 9.

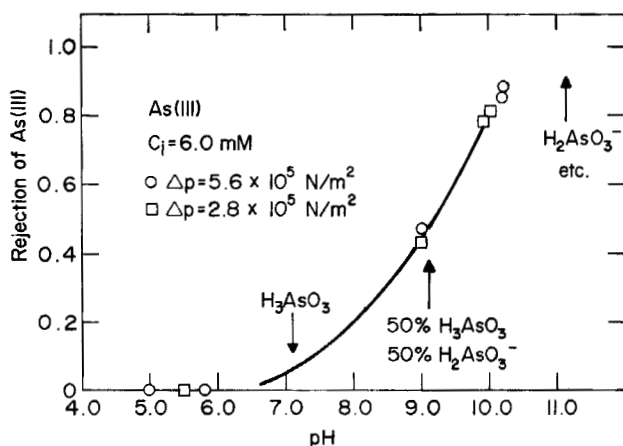


FIG. 5. Effect of pH on rejection of As(III).

of 6.0 mM, over pH 5 to 10, and at transmembrane pressure differences of 2.8×10^5 and $5.6 \times 10^5 \text{ N/m}^2$. Figure 5 shows that zero rejection of As(III) at H_3AsO_3 was achieved at pH 5 to 6. The species distribution was established from the first dissociation constant of H_3AsO_3 , $K = 8.1 \times 10^{-10}$ (6). Zero rejection of the noncharged species would be expected; As(III) as H_3AsO_3 could thus be separated from As(V) as H_2AsO_4^- by ultrafiltration at pH 4 to 6. The rejection increased to 0.85 at pH 10+, at which H_2AsO_3^- was the predominant species (some HAsO_3^{2-} was also present). As(III) could be ultrafiltered from a non-ferrous metals production waste or process stream after pH elevation to 10; however, operation at pH 5 would not be precluded due to the oxidation by dissolved oxygen or other oxidizing agents of As(III) \rightarrow As(V).

The final series of single-salt experiments investigated CdSO_4 solutions at a feed stream metal concentration of 6.0 mM, at pH 5, and at transmembrane pressure differences of 2.8×10^5 and $5.6 \times 10^5 \text{ N/m}^2$. At the lower Δp the rejection of Cd(II) (and thus of sulfate) was 0.90, and at the higher Δp the rejection was 0.92. Similar results were reported (2, 3) for CuSO_4 , NiSO_4 , and ZnSO_4 , with metal rejections of 0.88 at $\Delta p = 2.8 \times 10^5 \text{ N/m}^2$. The sulfate rejection in the presence of Cd(II) was somewhat lower than that in the presence of sodium ($R = 0.95$, from Fig. 4 at $C_i = 6.0 \text{ mM}$); this would be expected from Donnan theory on the basis of counterion valency.

A summary of single-salt rejection data for the most typical constituents

of nonferrous metals production streams is given in Table 2, at an initial metal (or sulfate) concentration of 6.0 mM and at pH 5. An additional series of ultrafiltration experiments was carried out with NaF, NaCl, NaNO₃, NaBr, NaI, or NaClO₄, each at 3.0 mM, pH 5, and $\Delta p = 2.8 \times 10^5$ N/m², to compare the rejections of monovalent H₂AsO₄⁻ and HSeO₃⁻ with those of the halides and other common oxyanions. Results are shown in Table 3. The oxyanions H₂AsO₄⁻ and HSeO₃⁻ could thus be separated by ultrafiltration from a stream also containing Cl⁻, Br⁻, I⁻, NO₃⁻, and/or ClO₄⁻ with a substantial fraction of these latter species passing through the membrane and thereby preventing the existence of the large effective osmotic pressures differences which would correspond to the high rejections of all ionic species produced in reverse osmosis. In addition, some selective separation of H₂AsO₄⁻ and HSeO₃⁻ from the other anions (except F⁻) could be accomplished.

For the entire series of single-salt experiments (and also for the multi-

TABLE 2
Summary of Single-Salt Rejections at $C_i = 6.0$ mM and pH 5

	Rejection	
	$\Delta p = 2.8 \times 10^5$ N/m ²	$\Delta p = 5.6 \times 10^5$ N/m ²
As(V): NaH ₂ AsO ₄	0.83	0.88
Se(IV): NaHSeO ₃	0.75	0.85
Sulfate: Na ₂ SO ₄	0.95	0.95
Cd(II): CdSO ₄	0.90	0.92
Zn(II): ZnSO ₄ (3)	0.88	—

TABLE 3
Single-Salt Rejections of Several Anions at $C_i = 3.0$ mM, pH 5, and $\Delta p = 2.8 \times 10^5$ N/m²

		Rejection
	NaH ₂ AsO ₄	0.84
	NaHSeO ₃	0.79
NaF		0.70
NaCl		0.43
	NaNO ₃	0.33
NaBr		0.29
NaI		0.25
	NaClO ₄	0.19

salt experiments described below), the water flux through the membrane, J_w , could be calculated from

$$J_w = \frac{\Delta p - \Delta \Pi}{R_m} \quad (4)$$

in which Δp is the transmembrane pressure difference, $\Delta \Pi$ is the effective osmotic pressure difference, and R_m is the membrane resistance for solute-free water. Equation (4) is applicable in the absence of concentration polarization: no concentration polarization was evident at the channel velocity of 167 cm/sec that was utilized throughout the experiments. The effective osmotic pressure difference was calculated from

$$\Delta \Pi = iC_i R' T R \quad (5)$$

in which i is the ionization factor, R' is the gas constant, and T is the absolute temperature. For example, the calculated $\Delta \Pi$ for 20 mM Na_2HAsO_4 was $0.98 \times 10^5 \text{ N/m}^2$, giving $J_w = (5.6 \times 10^5 - 0.98 \times 10^5) / 4.5 \times 10^8 = 1.0 \times 10^{-3} \text{ cm/sec}$ (Eq. 4). The calculated values of J_w were consistently close to the experimental values.

Multisalt Solutions at pH 5

The feed streams utilized in this phase of the investigation were similar to those that would be encountered in the nonferrous metals production industry. The first series involved the sodium salts of H_2AsO_4^- , HSeO_3^- , and SO_4^{2-} at transmembrane pressure differences of 2.8×10^5 and $5.6 \times 10^5 \text{ N/m}^2$. Results are presented in Table 4 for As(V) and Se(IV) in the presence and absence of sulfate. The As(V) and Se(IV) rejections for the mixture in the absence of sulfate were about the same as those

TABLE 4

Rejections of As(V) and Se(IV) Monovalent Oxyanions from Mixtures in the Absence and Presence of Sulfate at pH 5

	Rejection			
	$\Delta p = 2.8 \times 10^5 \text{ N/m}^2$		$\Delta p = 5.6 \times 10^5 \text{ N/m}^2$	
	As(V)	Se(IV)	As(V)	Se(IV)
3.0 mM H_2AsO_4^-				
+ 3.0 mM HSeO_3^-	0.87	0.75	0.90	0.85
Same + 10.0 mM SO_4^{2-}	0.84	0.73	0.90	0.84

reported above for single-salt solutions. The addition of 10.0 mM sulfate produced a quite small, negative effect on the rejections of As(V) and Se(IV) monovalent oxyanions. As analogous effect of SO_4^{2-} or of HPO_4^{2-} on the rejection of HCO_3^- had been reported previously (1, 2).

The second series of multisalt experiments established the effect of Cd^{2+} , as the sulfate, on the rejection behavior of H_2AsO_4^- and HSeO_3^- . The feed solutions were 3.0 mM in H_2AsO_4^- , 3.0 mM in HSeO_3^- , and from 0.04 to 3.0 mM in CdSO_4 , and Δp was $5.6 \times 10^5 \text{ N/m}^2$. Figure 6 shows the effects of the CdSO_4 concentration on the rejection of Cd(II), As(V), and Se(IV). The As(V) rejection declined from 0.90 to 0.78, but the Se(IV) rejection decreased sharply from 0.85 to 0.60. The effect, which was not produced by sulfate (see Table 4), could have been partly produced by the presence of the divalent Cd^{2+} (in contrast to just Na^+) according to Donnan theory, but most likely was brought about by some interaction in solution between Cd^{2+} and HSeO_3^- to form a soluble complex.

The final series of multisalt experiments determined the effect of the high concentrations of sulfate (as Na_2SO_4) frequently occurring in nonferrous metals production streams on the rejection behavior of a mixture containing H_2AsO_4^- , HSeO_3^- , Cd^{2+} , and Zn^{2+} . The feed streams were 2.0 mM in each metal and Δp was $5.6 \times 10^5 \text{ N/m}^2$. Figure

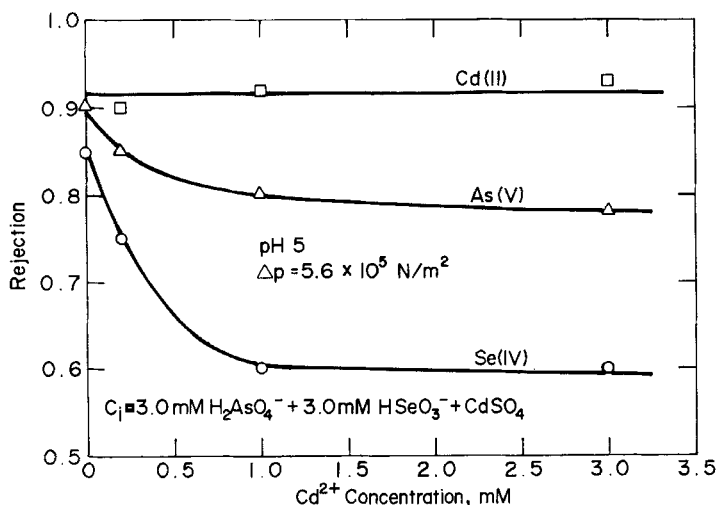


FIG. 6. Effect of Cd^{2+} (as the sulfate) concentration on rejections of Cd(II), As(V), and Se(IV) from multisalt solutions at pH 5.

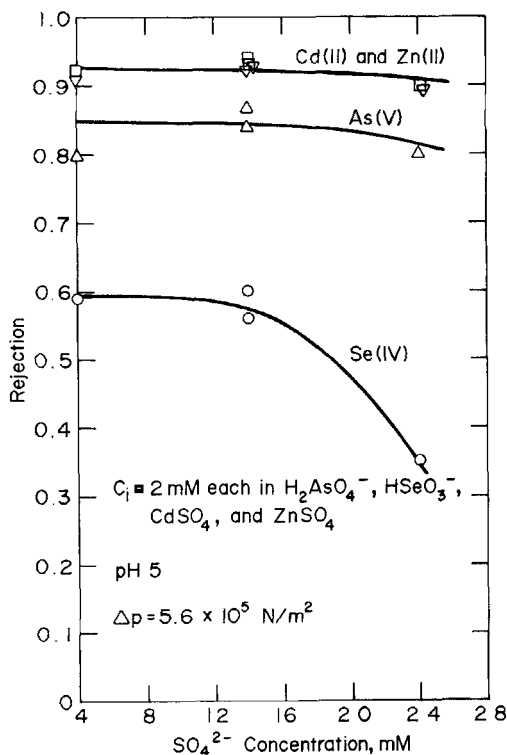


FIG. 7. Effect of sulfate concentration on rejections of Cd(II), Zn(II), As(V), and Se(IV) from multisalt solutions at pH 5.

7 indicates that the sulfate concentration in the feed stream had very little effect on the rejections of Cd(II), Zn(II), and As(V), but with an increase in sulfate from 14 to 24 mM, the Se(IV) rejection decreased from 0.58 to 0.35.

For a nonferrous metals production stream containing 2.0 mM H_2AsO_4^- , 2.0 mM HSeO_3^- , 2.0 mM Cd^{2+} , 2.0 mM Zn^{2+} , and a total of 14.0 mM SO_4^{2-} , charged membrane ultrafiltration at pH 5 would result in Cd(II) and Zn(II) rejections of 0.93, As(V) rejection of 0.85, Se(IV) rejection of 0.58, and sulfate rejection of 0.95. The ultrafiltrate stream would be 0.14 mM in Cd(II) and Zn(II), 0.30 in As(V), 0.84 in Se(IV), and 0.70 in sulfate, and the water flux would be $0.9 \times 10^{-3} \text{ cm/sec}$ (compared to the solute-free flux of $1.2 \times 10^{-3} \text{ cm/sec}$). Lower concen-

trations in all species, particularly of As(V) and Se(IV), could of course be achieved by operation at an elevated pH or by passing the ultrafiltrate through one additional ultrafiltration unit.

CONCLUSIONS

Single-salt solutions of As(V), Se(IV), As(III), or Cd(II) were ultrafiltered, using charged, noncellulosic membranes of resistance 4.5×10^8 N/m²/cm/sec, over pH 5 to 10, with metal concentrations in the range 0.5 to 20 mM, and at transmembrane pressure differences of 2.8×10^5 to 5.6×10^5 N/m². For As(V) and Se(IV), the rejections of divalent oxyanions (pH 9) were greater than those for the monovalent species (pH 5), rejections increased with increases in the transmembrane pressure difference, particularly for monovalent oxyanions, and the rejections were decreasing power functions of the feed stream concentrations. For As(III), the rejection of H₃AsO₃ was zero at pH 5 to 6 but the rejection of H₂AsO₃⁻ was 0.85 at pH 10. For Cd(II) as the sulfate, the rejection was 0.91, similar to other heavy metals such as Zn(II). At pH 5, the rejections of H₂AsO₄⁻ and HSeO₃⁻ were 0.84 and 0.79, respectively, at a feed stream concentration of 3.0 mM and a transmembrane pressure difference of 2.8×10^5 N/m², compared to rejections of Cl⁻, NO₃⁻, I⁻, and ClO₄⁻ (all sodium salts) of 0.43, 0.33, 0.25, and 0.19, respectively. The water flux was predictable on the basis of the transmembrane pressure difference, effective osmotic pressure difference, and the assumption of no concentration polarization.

Multisalt solutions of As(V) and Se(IV) at pH 5 evidenced rejections similar to those of the single-salt solutions and were not markedly influenced by the presence of sulfate. CdSO₄ produced a substantial decrease in the rejection of Se(IV), probably due to Cd²⁺-HSeO₃⁻ interaction. A very high (24 mM) sulfate concentration did not influence the rejections of Cd(II), Zn(II), and As(V) in a multisalt solution 2.0 mM in each of the four metals at pH 5, but produced a marked decrease in the Se(IV) rejection compared to a 14 mM sulfate concentration. The overall results were promising for the treatment of nonferrous metals production waste streams by charged membrane ultrafiltration for the reduction in concentrations of toxic metals and for ultrafiltrate use.

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