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Use of Electrodialysis to Remove Heavy Metals from Water

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Abstract

The removal of heavy metals from water by using electrodialysis is discussed. Parameters studied include current efficiency, stack resistance, and osmotic water transfer. Four single-electrolyte systems are investigated: $CdCl_2$ and $CdSO_4$ are used as representative heavy metal salts; NaCl and $CaCl_2$ are studied in order to enhance the understanding of physical electrodialytic processes in general and to provide a basis of comparison. The variables of electrolyte type, electrolyte concentration, pH, temperature, and elapsed time of membrane usage are examined. Results indicate that the purification of cadmium-laden waters can be achieved while maintaining high current efficiencies and reasonable stack resistances. The osmotic water transfers (in units of liter/mole) of the above cadmium salts are small enough to allow a high percentage of a wastewater stream to be reclaimed as purified water, but are higher than the water transfers of NaCl and $CaCl_2$ due to increased hydration effects.

INTRODUCTION

In recent years, heavy metal electrolytes have gained attention because of their potential for being both toxic and valuable. This dual potential often makes the clean-up of aqueous heavy metal streams economically desirable if not mandatory. Silver, cadmium, and mercury are examples of valuable heavy metals that the Environmental Protection Agency considers to be toxic when present as low-level ions in solution, as discussed by Eisenberg and Middlebrooks (*1*).

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Electrodialysis (ED) is a membrane-based separation technique that is appealing because of its capability to deionize one stream while concentrating the electrolyte(s) in another stream. Thus, ED produces a purified stream that can be either discharged or reused, and a concentrated electrolyte stream that can be disposed or processed for reclamation of the dissolved salt. Some applications of electrodialysis include desalination of brackish waters (*2–4*), desalting of whey and stabilization of wine (*5*), purification of protein solutions (*6*), recovery of metals from metal plating rinse waters (*7, 8*), recovery of acids (*9–11*), and recovery of heavy metals from mining mill process waters (*12*).

This report is concerned with the removal of $CdCl_2$ and $CdSO_4$ from water by use of electrodialysis. The effects of electrolyte type, electrolyte concentration, pH, temperature, and elapsed time of membrane usage upon current efficiency and membrane stack resistance are examined. Also, osmotic water transfers are presented for NaCl, $CaCl_2$, $CdCl_2$, and $CdSO_4$. The inclusion of NaCl and $CaCl_2$ in these studies was done to improve the understanding of the mechanisms of cadmium removal. Only single-electrolyte systems were investigated in this study.

Since the purpose of this work is to determine the technological feasibility of removing heavy metals from water by using ED, explicit studies in design optimization and economics are not pursued here. However, the relationships between measured design parameters and capital and operating costs are discussed.

GENERAL BACKGROUND

Electrodialysis is a separation technique that accomplishes the deionization of water streams by using a series of ion-exchange membranes bound by two electrodes, and a direct current electrical potential gradient as the driving force. Being a flexible unit operation, ED can be operated in a batch, semibatch, or continuous mode.

The actual transfer of ions occurs in the membrane module or *stack*. The membrane stack configuration used in this work is illustrated in Fig. 1, and will be referred to as the heavy metal stack. This stack consists of a collection of alternating cation-exchange and anion-exchange membranes that are placed between an anode and a cathode. Ion-exchange membranes typically consist of a crosslinked polymer matrix to which positive functional groups (for anion transfer) or negative functional groups (for cation transfer) have been chemically bonded. As a voltage is applied to the electrodes, cations are able to pass through cation-exchange membranes enroute to the negative cathode, but are repulsed

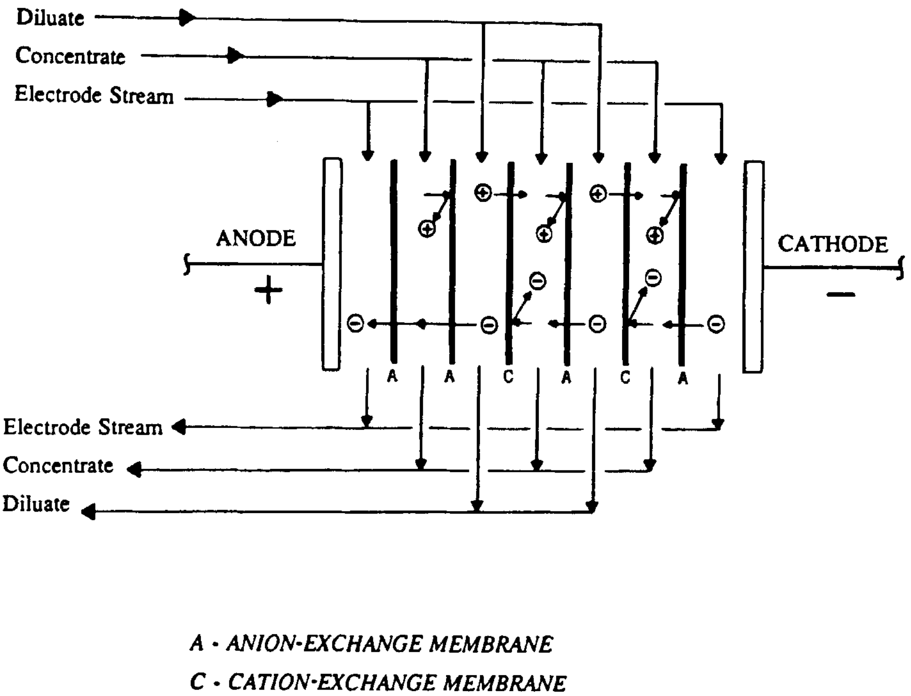


FIG. 1. ED stack configuration used for heavy metal removal.

upon encountering an anion-exchange membrane. Likewise, anions migrate toward the positive anode and are able to pass through anion-exchange membranes, but are prohibited from passing through cation-exchange membranes. The membranes generally have inert perforated spacers between them to provide structural support, to direct the streams to their appropriate flow channels, and to promote turbulent flow of all streams within the stack. The sequence of [cation-exchange membrane, spacer, anion-exchange membrane, spacer] is defined as a *cell pair*. Note that the heavy metal stack has two cell pairs plus one isolating compartment (two anion-exchange membranes in series separated by a spacer). Membranes that are part of an isolating compartment are generally excluded from the cell pair count (*13*). Commercial ED stacks can contain several hundred cell pairs, and multiple stacks may be incorporated into a single deionization operation.

As a result of the above selective transfer of ions there arises a stream that becomes increasingly depleted of electrolyte, the *diluate*, and a stream that becomes increasingly enriched with electrolyte, the *concentrate.* A third stream present in the stack is the *electrode* stream, which acts to rinse and protect the electrodes. The diluate will ultimately become the purified stream that can be recycled as process water or discharged according to effluent specifications. Similarly, the concentrate stream will eventually contain sufficient amounts of recovered electrolyte to enable either recycle (e.g., metal plating baths) or disposal at a cost much less than the disposal cost of an untreated wastewater stream.

EXPERIMENTAL

Description of Apparatus

A process flow diagram of the experimental ED unit is given in Fig. 2. This unit, a modified Chemomat Stackpack model manufactured by Ionics, Incorporated, can be operated in a batch or semibatch mode. The diluate, concentrate, and electrode streams flow from their respective holding tanks, are pumped through rotameters, and enter the membrane stack. Upon exiting the stack, the streams are recycled to their holding tanks. Note that the electrode stream is split before entering the stack, thus providing identical catholyte and anolyte feed streams. Samples can be taken via sample valves (V1) preceding the pumps. In-line pressure gauges are included, as well as temperature indicators, cooling coils, and mixers for the holding tanks. Finally, a Beckman Tech 300 multimeter was used to facilitate more accurate voltage readings.

Membrane Stack Components and Considerations

The heavy metal stack used in this work (see Fig. 1) is a 9 × 10 in. tortuous flow model that contains two cell pairs, one isolating compartment, and a set of electrodes. This assembly is compressed between metal plates by using tie rods. The anode consists of platinum-coated columbium and the cathode is made of Hastelloy. To lessen evaporative losses, polyethylene tape was wrapped around the stack where the exposed edges of the membranes were visible.

The membranes utilized in the stack are Ionics cation-exchange membrane 61-CZL-386 and Ionics anion-exchange membrane 103-QZL-386. These are "medium pore sized" homogeneous membranes that have an effective cell pair area (ECPA) of 220 cm^2. ECPA is defined as half the

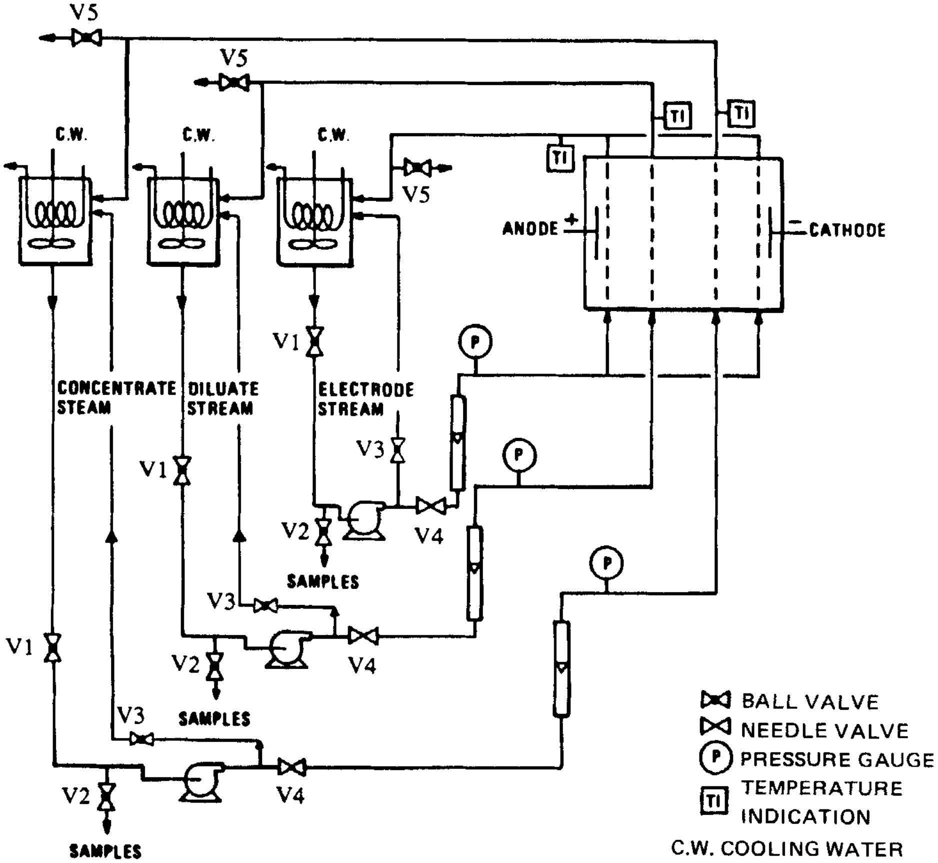


FIG. 2. Process flow diagram of experimental electrodialysis unit.

area of a cell pair that is available for effective ion transfer. Table 1 contains a listing of important membrane properties reported by the membrane manufacturer.

The above ion-exchange membranes are composed of a polymer matrix (polystyrene with polydivinylbenzene crosslinks) on a modacrylic reinforcing fabric. Quaternary ammonium groups serve as exchange sites for the anion-exchange membranes, and sulfonate groups are the exchange sites for the cation-exchange membranes. Ionics membranes have been shown to be chemically and thermally stable under prolonged harsh conditions (*14*).

The membrane configuration of the heavy metal stack allows a

TABLE 1
Membrane Properties

Membrane type	103-QZL-386	61-CZL-386
Weight, g/m^2	136	136
Thickness, mm	0.63	0.60
Burst strength, kPa	965	793
Water content based on wet resin, %	36	40
Ion-exchange capacity, mequiv/g of dry resin	2.1	2.7

common anion to be present in all three streams. A *common ion* is defined as the ion (cation or anion) present in the diluate, concentrate, and electrode streams by virtue of the stack design. Having a heavy metal cation present in the electrode stream is undesirable because the heavy metal can plate onto the cathode. Shaffer and Mintz (*15*) warn of such metal reduction.

Under normal operation there exists sufficient voltage to promote the formation of gasses such as O_2, H_2, and Cl_2 at the electrodes, as discussed later.

Operating Conditions

All experimental runs were done in a batch mode during which the stack voltage, flow rates, and temperature were kept constant. The voltage applied to the stack was 4 V/cell pair (8 V total) exclusively, which generated current densities ranging from 0.1 to 45 mA/cm^2. Typical voltages for commercial desalination units are around 2 V/cell pair (*16*). Constant-voltage modes have been found to be preferable over constant-current modes for batch units (*15*, *17*).

The linear velocity of flow through the stack was 35 ± 2 cm/s, producing a Reynolds number of about 600. Common linear velocities for tortuous flow designs are 30 to 50 cm/s (*18*) but velocities up to 100 cm/s have been reported (*13*). The fluid pressures of all three streams were set equal (15 psig) to prevent membrane stressing or cracking. Constant-temperature operation was achieved by using cooling coils placed in the tanks, resulting in stream temperatures of 78 ± 2°F, except for a few runs where 90 ± 2°F was used. Duration of the experimental runs, i.e., the net time that voltage was applied to the stack, ranged from 2.5 to 7 h. At timed intervals during a run, diluate and concentrate samples were taken, and current and temperature values were recorded.

The initial compositions of the diluate and concentrate were chosen according to the nature of the experimental run at hand. *Initial* is used here to indicate a stream condition at time zero during a run. When runs were performed to determine current efficiencies and stack resistances, the initial diluate concentration was approximately 0.05 M (mol/L) salt, and the initial concentrate ranged from 0.0 to 1.2 M salt. A *standard run* was arbitrarily defined as a run that had 0.05 M diluate and 0.0 M concentrate as initial stream concentrations. For osmotic water transfer studies, the diluate was 0.1 to 0.25 M and the concentrate range was the same as above.

Electrode stream compositions were formulated according to the goal of keeping the conductivity of the electrode stream constant between runs utilizing different common anions. When chloride was the common anion, the electrode stream was 0.2 M NaCl. However, 0.135 M Na_2SO_4 was used in the electrode stream when sulfate was the common anion.

An initial pH of 3.2 was chosen for the diluate and concentrate streams, except for a few special runs where no acid was added. The electrode stream had an initial pH of 1.7 to 2.1. HCl was used to adjust the pH for runs having chloride as the common anion, and H_2SO_4 was used when sulfate was the common anion. Acidification of all three streams was done so that scale formation and detrimental electrode reactions could be avoided. Acid treatment is commonly used in ED operations to inhibit harmful multivalent scales such as $Ca(OH)_2$, $CaCO_3$, $Mg(OH)_2$, etc. (*3*, *19–21*). In almost all cases the initial ratio of salt cation concentration to hydrogen ion concentration was at least 50:1 in both the diluate and concentrate. A ratio this large was chosen with the goal of preventing H^+ ions from interfering with current efficiencies by carrying a significant portion of the current.

All chemicals used in this work were reagent-grade stock ordered from Fisher Scientific. All solutions were prepared with distilled, deionized water. Special care was taken when handling acids and cadmium salts, since certain airborne cadmium salts are known to be severe respiratory irritants (*22*).

Analytical Procedure

Ion-specific electrodes were used to determine the concentrations of all salts and acids present in the samples. Fisher Scientific electrodes [models 13-639-20 and 13-639-52 (calomel reference)] were used for sodium ion concentration measurements. Cadmium ion concentrations were determined by an Orion cadmium specific electrode 94-48-00 with reference electrode 90-01-00. Similarly, calcium ion concentrations were determined by an Orion calcium specific electrode 93-20-00 with reference 90-01-00. pH measurements were obtained from a Fisher Scientific pH electrode 13-639-3 with calomel reference electrode 13-639-52, or from a Corning combination pH electrode 476182. The reference electrodes listed above are single junction models. The electrode meter used with all of the above electrodes was an Orion model 701A/digital Ionalyzer.

CONSIDERATIONS IN THE UTILIZATION OF ELECTRODIALYSIS

Design Parameters

Current Efficiency

For an electrodialytic process, current efficiency (η) is defined as the fraction of the current passing through a cell pair that accomplishes the net migration of desired ions from the diluate to the concentrate. Expressions for current efficiency can be derived from a material balance around an ED stack:

$$\eta = -\frac{F Vol_D \Delta C_D}{nI} \tag{1}$$

where F is Faraday's constant, Vol_D is the total diluate volume during the time interval Δt, ΔC_D is the change in the diluate electrolyte concentration (equivalents/liter) during Δt, n is the number of cell pairs, and I is the current over Δt as given by

$$I = \int_{t_1}^{t_2} i(t)\,dt \tag{2}$$

which can be evaluated by using a simple numerical technique on the $(i(t),t)$ data pairs.

Written as is, Eq. (1) does not account for the change in diluate volume that is due to osmotic water transfer across the membranes during the interval Δt. To account for this solvent transfer effect, $Vol_D \Delta C_D$ would actually have to be written as $\Delta(Vol_D C_D)$, but this is not done here because the water transfer was not continuously measured during runs that determined current efficiencies. Thus, the assumption that $Vol_D \Delta C_D \approx \Delta(Vol_D C_D)$ is made, resulting in calculated current efficiencies that have a relative error of less than 6% for the diluate concentration ranges considered in this work. The total experimental error encountered in this study ranges from about 2 to 8%, depending on experimental conditions. Current efficiencies can be based on concentrate stream conditions, but are generally less accurate than those based on diluate stream conditions.

Stack Resistance

Stack resistance is the sum total of all electrical resistances present within the stack at any given moment. These electrical resistances arise from both membrane and solution contributions, and can be viewed as a collection of resistors in series. The *apparent* stack resistance, R_a, is calculated from

$$R_a = \frac{V_a A}{nI} \tag{3}$$

where V_a is the total apparent or observed stack voltage, A is the effective cell pair area, and n and I are the same as above. R_a is an *area-specific* resistance, with typical units of ohm · cm^2.

Given a unit of membrane surface area, electrical resistances of ion-exchange membranes are dependent upon the species of electrolyte(s) present, electrolyte concentration, membrane temperature, and membrane thickness (*23–25*). These resistances are usually a minor contribution to the total stack resistance, but can increase in significance if the diluate and concentrate stream resistances are low due to high electrolyte concentration, as is the case in the production of salt from seawater by ED where about 40% of the total stack resistance can be attributed to membrane resistances (*21*). Area-specific membrane resistances are generally less than 20 ohm · cm^2 (*3*, *26*). Solution resistances likewise depend on the type and concentration of the electrolyte(s), solution temperatures, and solution compartment thicknesses (*3*, *16*). The electrical resistances of both solutions and membranes will increase if nonelectrolyte impurities, such as heavy organic molecules, act to impede the flow of current.

As stated above, an apparent stack resistance is calculated from an observed total stack voltage. However, true stack resistances (R_t) differ from apparent stack resistances in that they do not include resistances originating from electrode potentials and electrode overvoltages. However, determining values for ($R_a - R_t$) is no trivial task since the complex mechanisms and interplay between competing electrode reactions and overvoltages remain somewhat unclear. Due to this difficulty, apparent stack resistances are presented herein exclusively. It should be noted that R_t approaches R_a as the number of cell pairs increases.

Osmotic Water Transfer

Osmotic water transfer (OWT) refers to the net transfer of water that occurs by ion hydration effects and by gradients across an ion-exchange membrane (electrical, temperature, mechanical pressure, and concentration) that promote solvent transport through that membrane (*19*). Temperature and pressure gradients are negligible in most cases. Normal osmosis, caused by concentration gradients, is generally a small percentage of the total OWT. For example, the normal osmosis contribution for NaCl removed by ED has been found to be less than 5% of the total OWT, even at fairly high osmotic pressures (*11*). As a consequence, normal osmosis will no longer be considered here. Thus, OWT is due almost entirely to waters of hydration and electroosmosis when other gradients are absent.

The economic usefulness of an electrodialysis process is affected by the amount of water transfer that occurs, since OWT decreases the amount of diluate that can be reclaimed as process water and increases the amount of water in the concentrate. The ideal situation for water/electrolyte recovery is to have the osmotically transformed water as the only water present in the concentrate stream. The result would be that the net volume of the concentrate would be a small fraction of the diluate net volume. This minimized concentrate volume minimizes disposal costs or recycle pumping costs of the concentrate stream.

Economic Considerations

Now that design parameters have been carefully defined, they can be related to operating and capital costs. The total effective membrane area required for an ED process is directly related to capital costs. Energy costs can be a substantial fraction of operating costs in ED. If a unit volume of treated diluate is taken as a basis, the following relations can be obtained:

$$\alpha \propto -\frac{R_a \Delta C_D}{V_a \eta} \tag{4}$$

$$\beta \propto -\frac{V_a \Delta C_D}{\eta} \tag{5}$$

where α and β are the effective cell pair area and energy consumption per unit volume of diluate treated, respectively. Equation (4) is obtained by solving for nI in Eqs. (1) and (2) and setting the resultant expressions equal to each other. Equation (5) can be derived by dividing the expression for Vol_D from Eq. (1) into the basic direct current power requirement equation (power = V_aI).

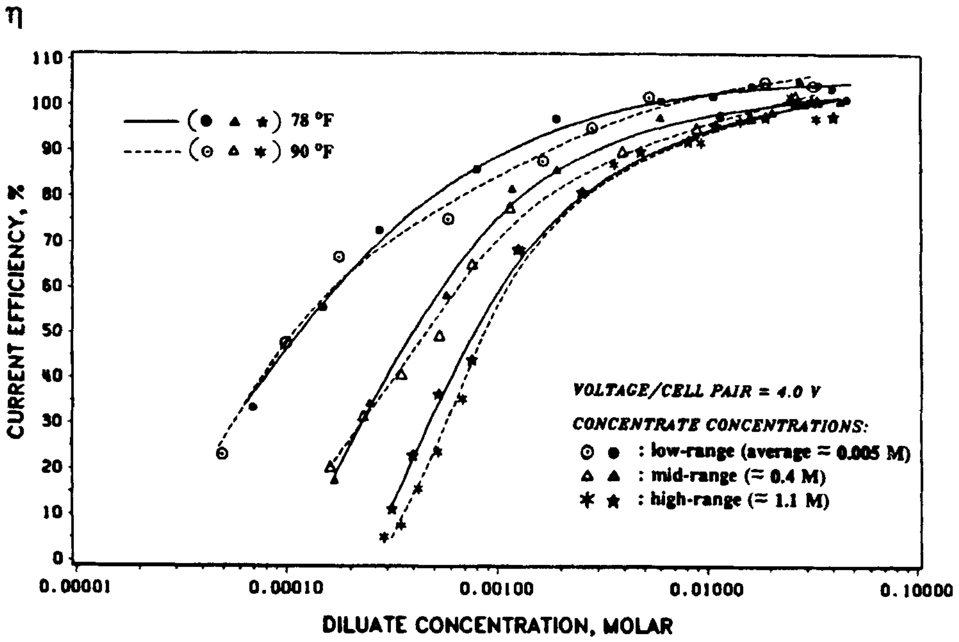
Since the applied stack voltage can be adjusted according to need, it is viewed as an independent operating variable. However, stack resistance and current efficiency are dependent upon V_a, and are therefore dependent operating variables. It is seen that α is inversely proportional to V_a, while β is directly proportional to V_a. Therefore, V_a is an independent variable that can be used to balance operating and capital costs in an economic optimization.

RESULTS

Current efficiency and stack resistance plots for $CdCl_2$ removal at 78 and 90°F are given in Fig. 3. Note that concentrate concentration is a variable in these plots, where each curve represents one experimental run. For these and other similar figures, the three concentrate concentration ranges shown will be referred to as *low-range* (average ≈ 0.005 *M*), *mid-range* or *moderate-range* (≈ 0.4 *M*), and *high-range* (≈ 1.1 *M*).

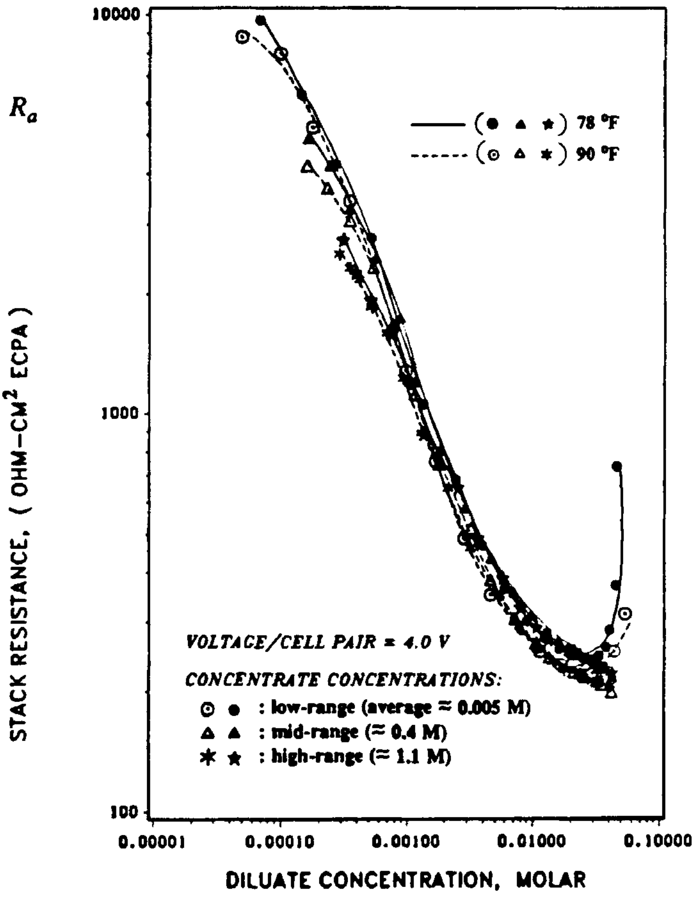
The current efficiency and stack resistance plots for $CdSO_4$ removal at 78°F are given in Fig. 4. A *low-level* run was substituted for a high-range concentrate run in these $CdSO_4$ studies. The purpose behind the low-level experiment was to characterize current efficiency and stack resistance plots for the removal of $CdSO_4$ from acidic solutions that have very low concentrations of heavy metals present in the diluate and concentrate. Such solutions can be found in rinse waters from electronic circuitry manufacturing, metal plating bath rinse waters, and some acid-mine drainage waters. Figure 5 shows the constituent and added current efficiencies for the low-level run.

To determine how the low-level run differed from runs having higher electrolyte concentrations, a run was conducted that had an initial

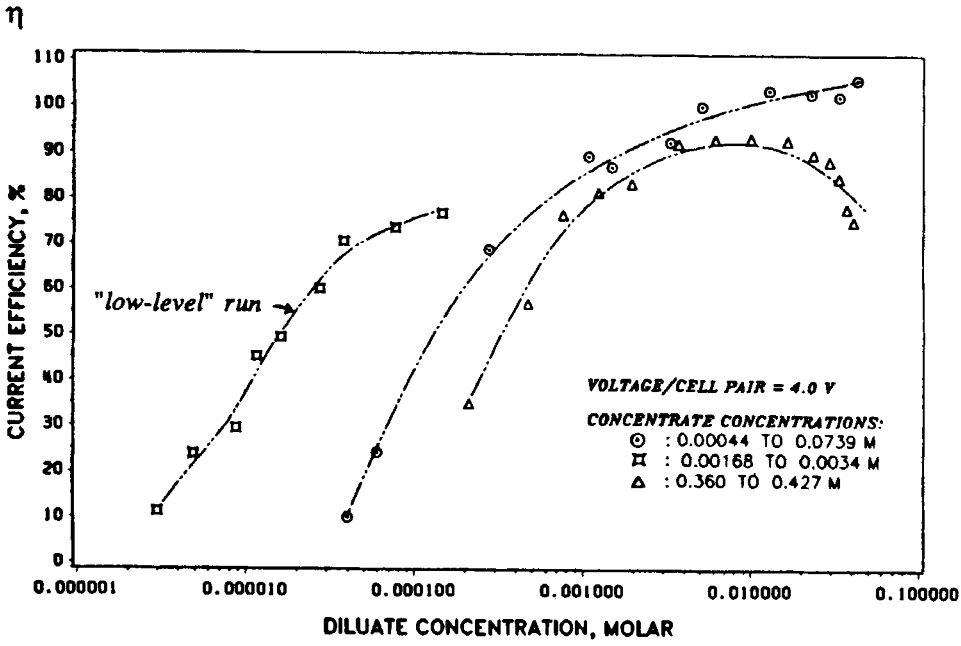


(a)

FIG. 3. Effect of electrolyte concentration and temperature on (a) current efficiency and (b) stack resistance plots of aqueous cadmium chloride solutions.

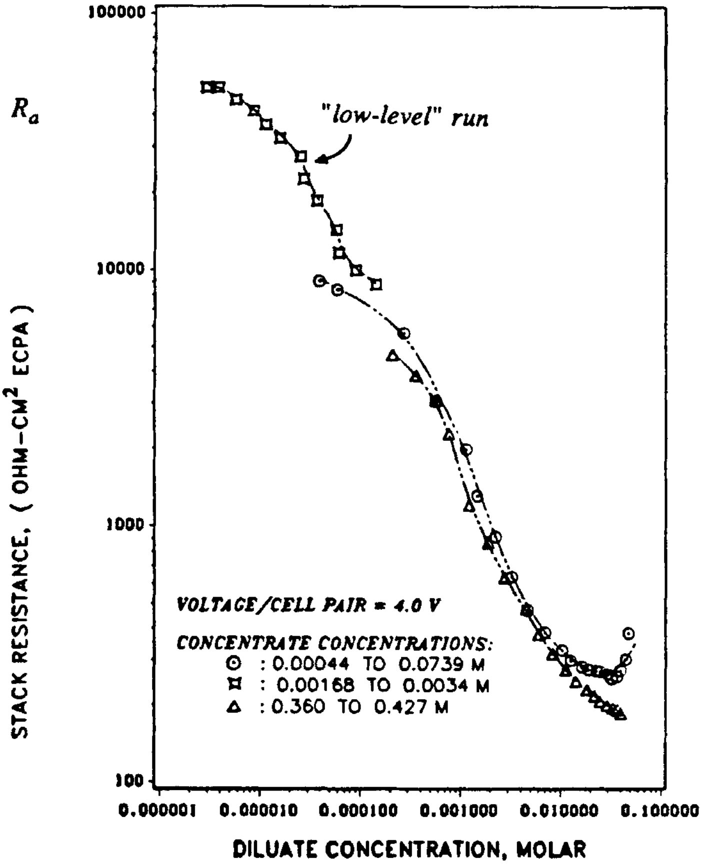

R_a
STACK RESISTANCE, (OHM-CM^2 ECPA)
10000
1000
100
0.00001
0.00010
0.00100
0.01000
0.10000
DILUATE CONCENTRATION, MOLAR
——— (● ▲ ★) 78 °F
------ (⊙ △ ✱) 90 °F
VOLTAGE/CELL PAIR = 4.0 V
CONCENTRATE CONCENTRATIONS:
⊙ ● : low-range (average ≈ 0.005 M)
△ ▲ : mid-range (≈ 0.4 M)
✱ ★ : high-range (≈ 1.1 M)

(b)



(a)

FIG. 4. Effect of electrolyte concentration on (a) current efficiency and (b) stack resistance plots of aqueous cadmium sulfate solutions, $T = 78°F$.


100000
10000
1000
100
R_a
STACK RESISTANCE, (OHM-CM^2 ECPA)
"low-level" run
VOLTAGE/CELL PAIR = 4.0 V
CONCENTRATE CONCENTRATIONS:
⊙ : 0.00044 TO 0.0739 M
⌑ : 0.00168 TO 0.0034 M
△ : 0.360 TO 0.427 M
0.000001
0.000010
0.000100
0.001000
0.010000
0.100000
DILUATE CONCENTRATION, MOLAR

(b)

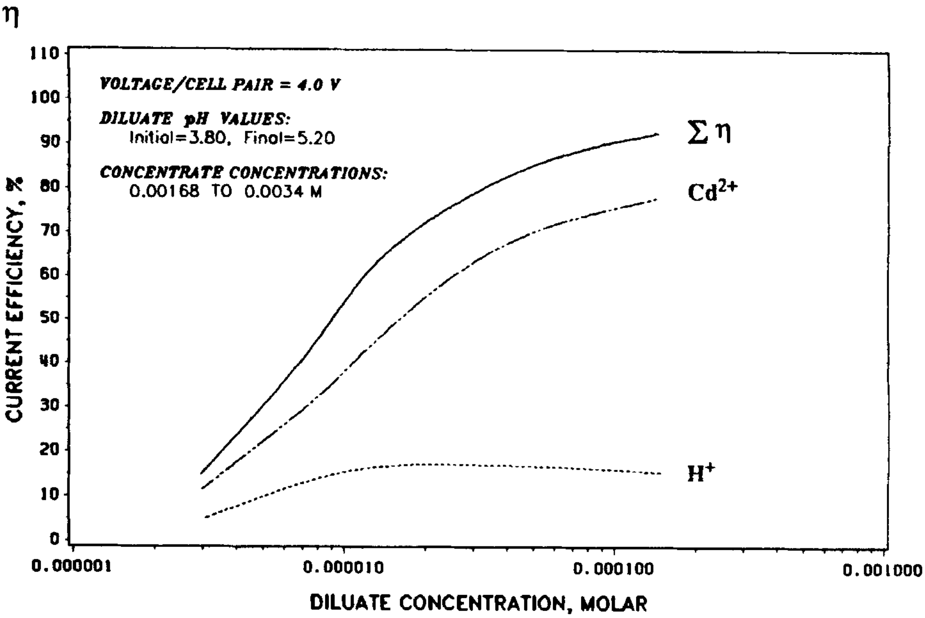


FIG. 5. Current efficiency plots of low-level cadmium sulfate solutions, T = 78°F.

concentrate/diluate molar ratio similar to that of the low-level run, but was approximately 200 times more concentrated in the initial diluate and concentrate streams. Results for this run and the low-level run are compared in Fig. 6, where current efficiency is plotted against the molar concentration ratio of concentrate/diluate.

The dependence of current efficiency and stack resistance upon both anion and cation type is shown in Fig. 7, which contains results for NaCl, $CdCl_2$, and $CdSO_4$ standard runs. Note that ionic strength is used as the abscissa. Using ionic strength instead of molarity is preferred in this case because ionic strength can better characterize the ionic concentrations of the 1:1, 2:1, and 2:2 electrolytes. The ionic strengths are calculated from the molar salt concentration only; the diluate and concentrate acid concentrations are not considered since they were a small fraction of the total electrolyte concentrations, and since they were very similar between these three standard runs.

The influence of diluate pH upon current efficiency and stack resistance is shown for $CdSO_4$ removal in Fig. 8. The initial diluate streams for the two runs represented in these two figures differed by approximately one pH unit.

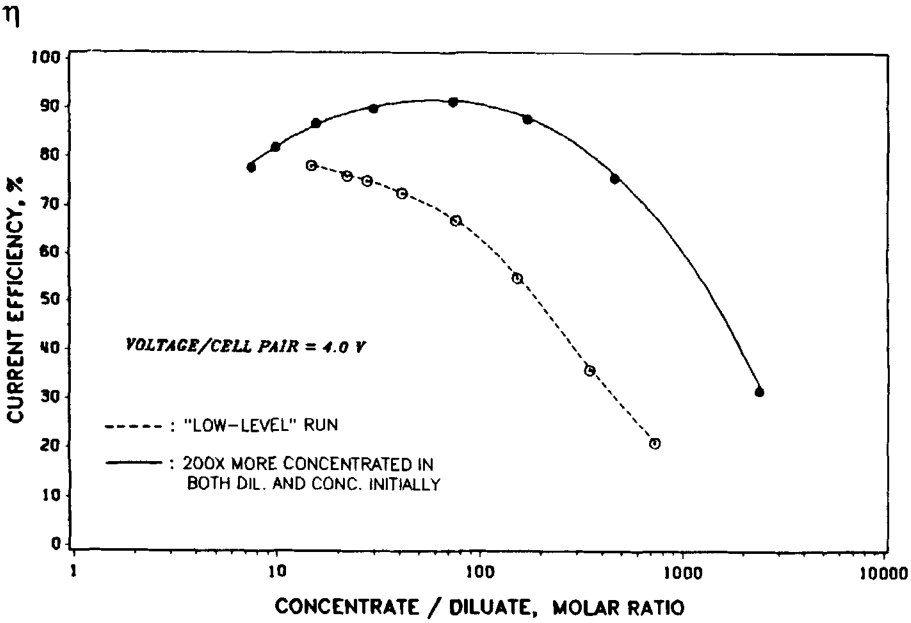


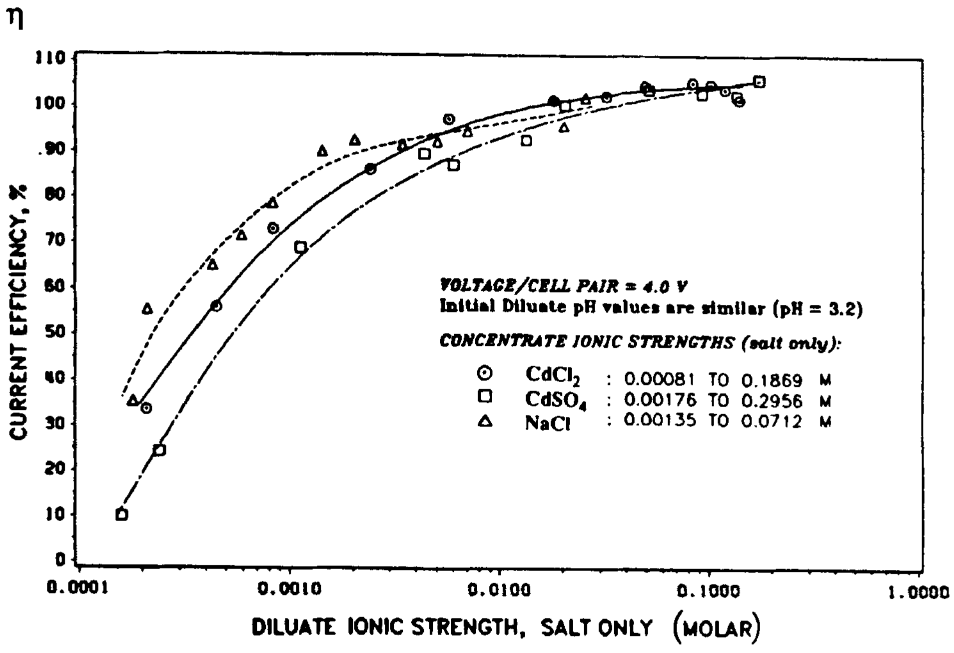
FIG. 6. Current efficiency plots of cadmium sulfate solutions with similar initial C/D ratios, but dissimilar initial concentrations. Solutions are at 78°F.

The elapsed time of membrane usage is considered in Fig. 9 in order to investigate membrane degradation. The current efficiencies and stack resistances shown are from three standard runs that were conducted at the indicated time intervals of membrane usage.

Experimental and theoretical osmotic water transfers are plotted against average molar concentrate concentrations in Fig. 10. Each of the experimental data points shown represents the water transfer that occurred over an entire run.

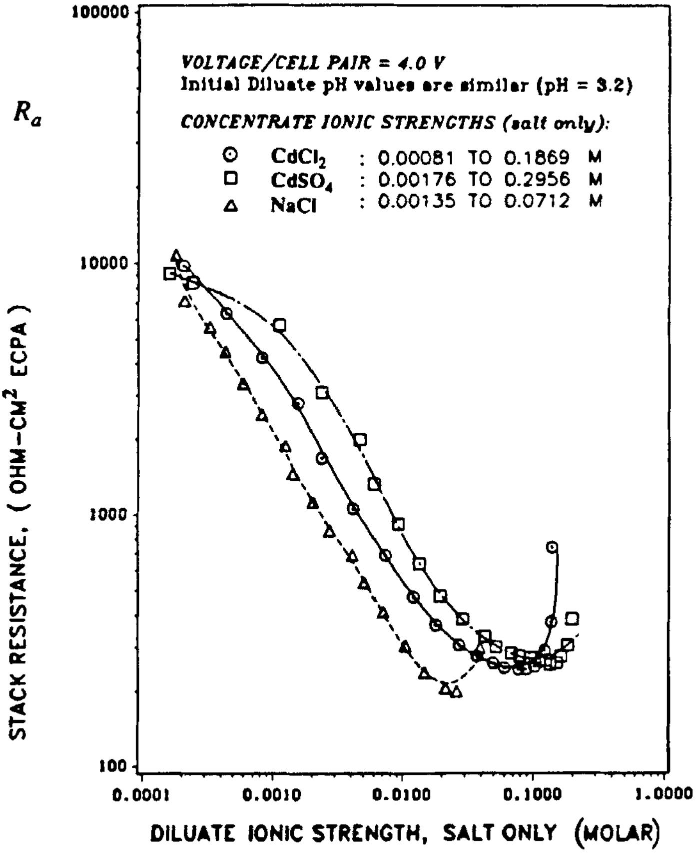
Since ion hydration is known to increase with decreasing electrolyte concentration (*27–29*) and since the average diluate electrolyte concentrations varied to a small extent between OWT runs employing a given salt, the experimental OWT values ($\mathrm{OWT}_{\mathrm{exp}}$) were *adjusted* with respect to a reference data point according to the relative cation hydration in the diluate. The resultant expression for the adjusted OWT ($\mathrm{OWT}_{\mathrm{adj}}$) is

$$\mathrm{OWT}_{\mathrm{adj}} = \mathrm{OWT}_{\mathrm{exp}} \left[\frac{v_r - v_a}{v_{\mathrm{exp}} - v_a} \right] \tag{6}$$

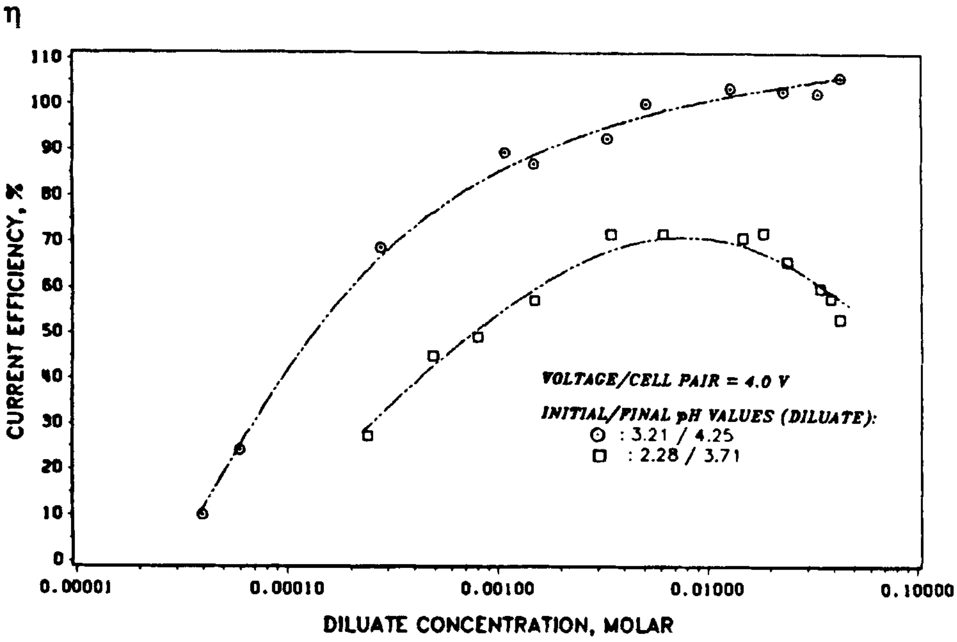


(a)

FIG. 7. Effect of electrolyte type on (a) current efficiency and (b) stack resistance plots of standard runs, T = 78°F.

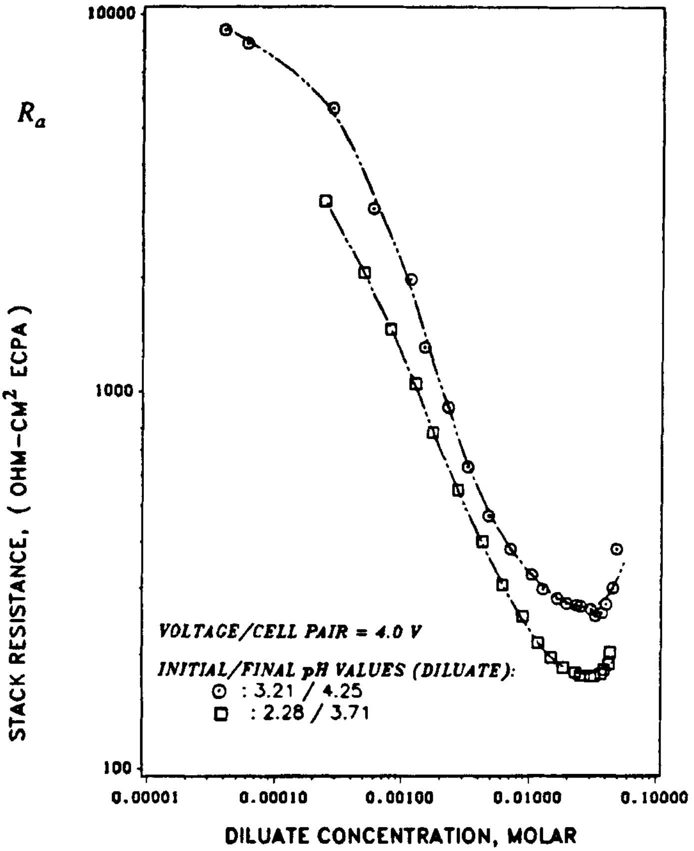

VOLTAGE/CELL PAIR = 4.0 V
Initial Diluate pH values are similar (pH = 3.2)
CONCENTRATE IONIC STRENGTHS (salt only):
○ $CdCl_2$: 0.00081 TO 0.1869 M
□ $CdSO_4$: 0.00176 TO 0.2956 M
△ NaCl : 0.00135 TO 0.0712 M
R_a
STACK RESISTANCE, (OHM-CM^2 ECPA)
100000
10000
1000
100
0.0001
0.0010
0.0100
0.1000
1.0000
DILUATE IONIC STRENGTH, SALT ONLY (MOLAR)

(b)

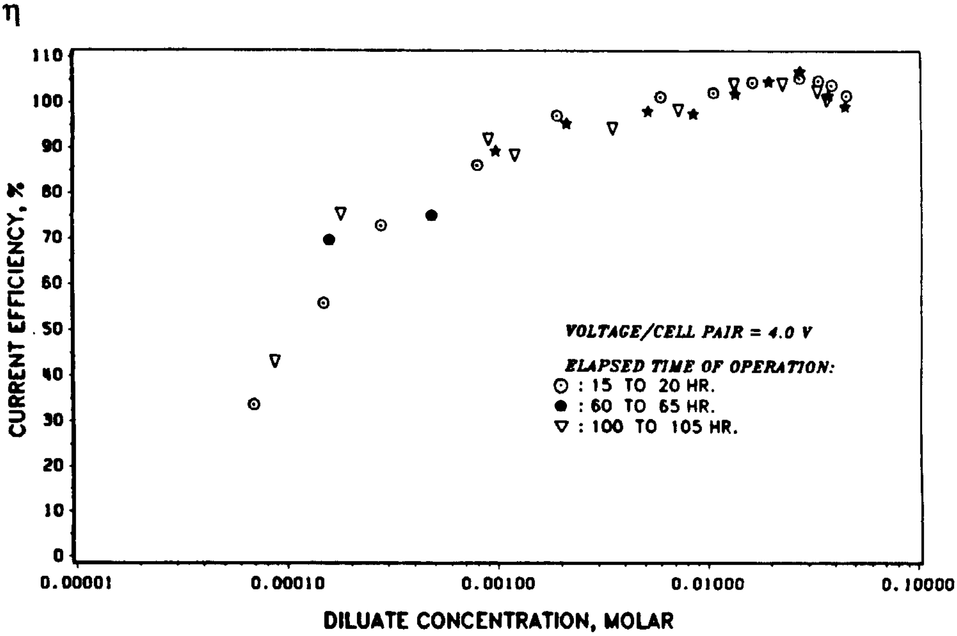


(a)

FIG. 8. Effect of pH on (a) current efficiency and (b) stack resistance plots of aqueous cadmium sulfate solutions at 78°F (similar concentrate concentrations).

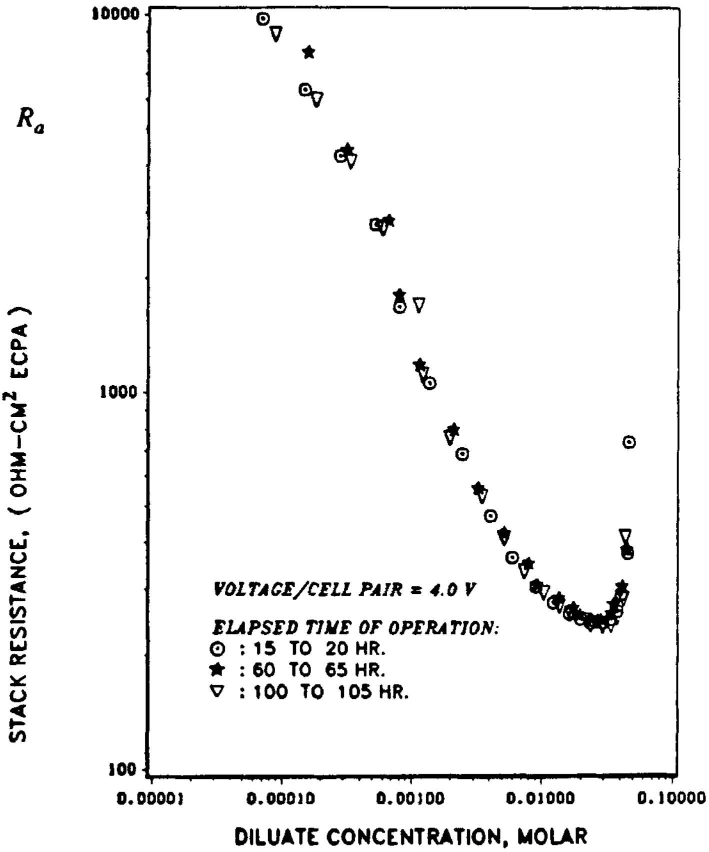

R_a
STACK RESISTANCE, (OHM-CM^2 ECPA)
10000
1000
100
0.00001
0.00010
0.00100
0.01000
0.10000
DILUATE CONCENTRATION, MOLAR
VOLTAGE/CELL PAIR = 4.0 V
INITIAL/FINAL pH VALUES (DILUATE):
⊙ : 3.21 / 4.25
□ : 2.28 / 3.71

(b)



(a)

FIG. 9. Effect of elapsed time of membrane usage on (a) current efficiency and (b) stack resistance plots of aqueous cadmium chloride solutions at 78°F (standard runs).


R_a
STACK RESISTANCE, (OHM-CM^2 ECPA)
10000
1000
100
0.00001
0.00010
0.00100
0.01000
0.10000
DILUATE CONCENTRATION, MOLAR
VOLTAGE/CELL PAIR = 4.0 V
ELAPSED TIME OF OPERATION:
⊙ : 15 TO 20 HR.
★ : 60 TO 65 HR.
▽ : 100 TO 105 HR.

(b)

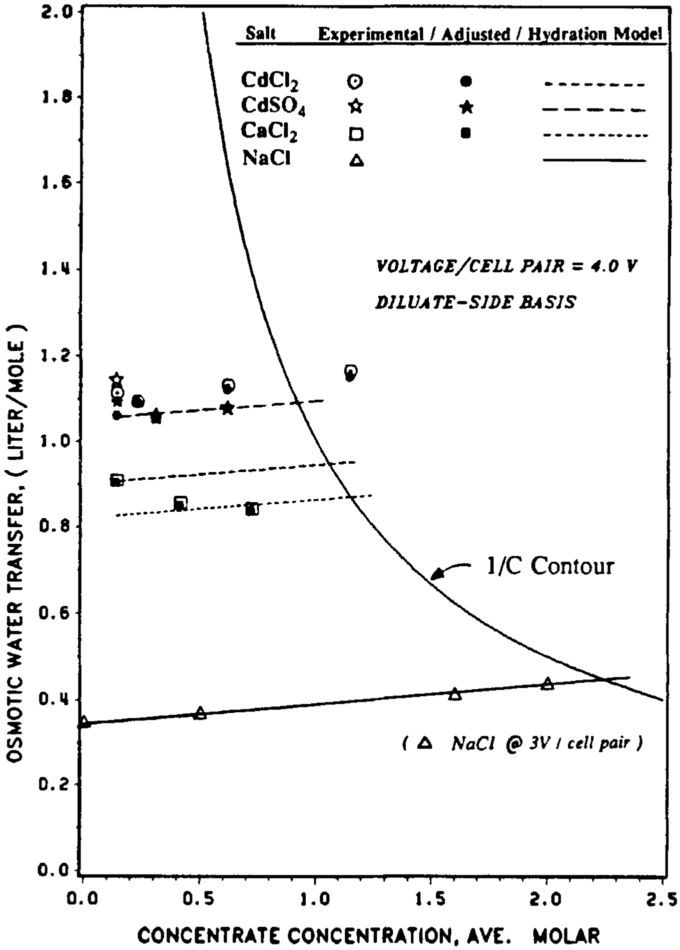


FIG. 10. Osmotic water transfers of various salt solutions at 78°F.

where

$$v_{r,a,\,\text{or exp}} = \frac{\pi d_+^3}{6} \qquad (7)$$

and where

$$d_+ = d_+^o + y\rho_+ + z\rho_+^2 \qquad (8)$$

The v_a term in Eq. (6) is the cation volume based on the cation atomic radii (i.e., nonhydrated volume), υ_{exp} is the hydrated cation volume at the average diluate concentration corresponding to $\mathrm{OWT}_{\mathrm{exp}}$, and υ_r is the hydrated cation volume at the average diluate concentration of the aforementioned reference data point, which is taken as the OWT data point that has the lowest average diluate concentration associated with it. The bracketed term in Eq. (6) can be thought of as a relative hydration ratio. Anion hydration is assumed to be constant over the range of diluate concentrations studied in this work.

Equation (8) is a quadratic expression for the hydrated cation diameter d_+ in terms of the hydrated cation diameter at infinite dilution d^o_+, the number density of the cation ρ_+, and a set of hydration parameters (y,z) that were derived by Landis (*30*), who used the MSA-EXP electrolyte model together with regression analysis to determine the hydrated cation diameter. The cation number density is defined as the number of cations per unit of volume, with typical units of $\mathrm{\AA}^{-3}$.

A simple linear *hydration model* was devised to evaluate the contribution that the waters of hydration give to the total OWT at a given concentrate concentration. The hydration model is based on the experimentally measured water transfers of an arbitrarily defined reference electrolyte, OWT_r, and the literature values for the experimentally determined hydration numbers of cations and anions at infinite dilution, h_i^∞. This model predicts the osmotic water transfer (OWT_h) for an electrolyte M_aN_b through the following expression:

$$\mathrm{OWT}_{h,M_aN_b} = m_r C_{M_aN_b} + \mathrm{OWT}_{r,C=0}\left[\frac{\left(\sum_{i=a}^{b} i h_i^\infty\right)_{M_aN_b}}{\left(\sum_{i=a}^{b} i h_i^\infty\right)_r}\right] \quad (9)$$

where m_r is the average slope of the OWT versus concentrate concentration curve for the reference electrolyte, C is the concentrate electrolyte concentration in molar units, and a and b are the moles of cations and anions, respectively, per mole of salt M_aN_b. For example, using NaCl as the reference and $\mathrm{CdCl_2}$ as M_aN_b:

$$\mathrm{OWT}_{h,\mathrm{CdCl_2}} = m_{\mathrm{NaCl}} C_{\mathrm{CdCl_2}} + \mathrm{OWT}_{\mathrm{NaCl},C=0}\left[\frac{(h^\infty_{\mathrm{Cd^{2+}}} + 2h^\infty_{\mathrm{Cl^-}})}{(h^\infty_{\mathrm{Na^+}} + h^\infty_{\mathrm{Cl^-}})}\right] \quad (10)$$

The h_i^∞ values used in this work are those given by Marcus (*28*). Table 2 contains a listing of hydration numbers and Eq. (8) parameters for the

TABLE 2
Equation (8) Parameters and Hydration Numbers

	Parameter			
	d^o_{+}, Å	y	z	h_i^∞
Na^+	3.575	−43.98	−9519.2	3.0
Ca^{2+}	5.912	−23.49	−48150.0	7.8
Cd^{2+}	5.443	−1334.8	0.0	9.0
Cl^-	—	—	—	2.3
SO_4^{2+}	—	—	—	6.9

ions considered here. NaCl was used as the reference electrolyte in Eq. (9) to obtain the OWT_h values shown in Fig. 10.

During the course of analysis of OWT data, it was often necessary to convert weight-based data into volume-based units. In order to preserve the accuracy of the data in such instances, a polynomial expression for the density of an electrolyte solution was used, which had molar electrolyte concentration and temperature as variables (*31*).

DISCUSSION

Current Efficiencies and Stack Resistances

The Effect of Electrolyte Concentration

Figures 3(a) and 4(a) show that current efficiency drops as the diluate concentration decreases and as the concentrate concentration increases. Simply stated, η decreases as the electrolyte concentration gradient increases between diluate and concentrate compartments. This is a well-documented phenomenon in ED (*9*, *11*, *17*, *26*, *32*).

When concentration polarization is absent, there are two main causes of this decrease in current efficiency: *co-ion intrusion* and *counterion backdiffusion*. Co-ion intrusion is the passage of co-ions (ions of the same charge as the membrane exchange sites) through an ion-exchange membrane from the concentrate to the diluate, and is due to the electrical potential and concentration gradients across that membrane. Counterion backdiffusion is the backward passage of counterions (ions having a charge opposite to that of the exchange sites) through an ion-exchange membrane from the concentrate to the diluate, due to a high concentration gradient across that membrane.

The effects of counterion backdiffusion can be lessened by increasing the stack voltage, that is, increasing the electrical potential driving force. However, such an increase in stack voltage is limited by the limiting current density (*3*, *33*), parasitic current losses in stack manifolds (*15*), and high energy costs (see Eq. 5). Co-ion intrusion can be reduced by using ion-exchange membranes that exclude co-ions to a greater degree.

Figures 3(b) and 4(b) show the dependence of stack resistance on electrolyte concentration. A decrease of diluate concentration is seen to have a greater effect upon stack resistance than a change in concentrate concentration. This is simply due to the higher resistivity (or lower conductivity) the diluate possesses because of its lower electrolyte concentration. The topmost plot (from a standard run) in each of these figures shows a "minimum" at the right-hand portion of the curve. This minimum is a point at which the diluate and concentrate concentrations are equal. The concentrate is more dilute than the diluate to the right of the minimum, but is more concentrated than the diluate to the left of the minimum.

Finally, when the current efficiency and stack resistance at a given diluate concentration are viewed simultaneously, it is evident that higher current efficiencies and lower stack resistances both correspond to higher diluate concentrations. Therefore, there is a trade-off between obtaining a low diluate effluent concentration while operating at favorable η and R_a.

The Effect of Electrolyte Type

Figure 7(a) shows that current efficiencies tend to increase in the following order: $CdSO_4 < CdCl_2 < NaCl$. At a given diluate and concentrate concentration, the difference in current efficiency plots in Fig. 7(a) is probably due to different transport numbers of the various ions. The transport number of an ion is defined as the fraction of current an ion carries in a solution compartment or membrane, and is a function of the ionic mobilities (velocity of an ion under a potential gradient) present in these solutions or membranes (*16*). Sulfate ions, being larger and more hydrated than chloride ions, may tend to have lower mobilities through solutions and membranes, thus causing lower transport numbers that would ultimately result in lower current efficiencies. Cadmium ions, being larger than sodium ions, would be more likely to exhibit lower mobilities, which would also result in lower current efficiencies.

The difference in stack resistance between the electrolytes shown in

Fig. 7(b) is due mostly to differences in resistivities between diluate streams containing these electrolytes. As should be expected, stack resistances are seen to increase in the order $NaCl < CdCl_2 < CdSO_4$. This order agrees with the resistivity data given by Dean (*34*). It should be noted that the resistance plots tend to converge (near 10,000 ohm · cm^2) as the diluate becomes more dilute. Such convergence should occur since the resistivity of any electrolyte solution approaches the resistivity of pure water as the electrolyte concentration falls to zero.

The trends seen in Figs. 7(a) and 7(b) are still observed if *normality* is used as the abscissa instead of ionic strength.

The total sodium in final concentrate solutions was found to be less than 1% of the sodium that was in the initial electrode stream. Likewise, the diluate usually contained less than 1% of the Na^+ in the concentrate. It is therefore concluded that sodium leakage from the electrode compartments to the concentrate and diluate compartments was not significant enough to affect current efficiencies and stack resistances for the experiments described here.

The Effect of Temperature

Figure 3 shows that an increase in stream temperature results in lower current efficiencies and lower stack resistances. These trends are in agreement with literature that has discussed the use of ED at elevated temperatures, where an increase in temperature has been seen to decrease R_a (*35*) while decreasing η (*36*). More recently, studies have been performed where temperature has been used as a true optimization variable (*37*). Stream temperature can be raised by utilizing an external heat source and/or by using the electrical resistance heat (the *Joule* heat) together with the heat generated by frictional fluid flow.

The drop in current efficiencies seen in Fig. 3(a) may be due in part to an enlargement of membrane pores as the temperature is increased. Larger pore diameters would contribute to increased co-ion intrusion, leading to decreased current efficiencies.

Electrical resistances of ion-exchange membranes will vary according to the chemical environment they are in, but will decrease with increasing temperature at an approximate rate of 1.8%/°C or 1%/°F (*3*). Similarly, the electrical resistances of saline solutions decrease with increased temperature by about 2%/°C (*15*). Thus, if an overall decrease of 1%/°F is chosen for both membranes and solutions, there should be a resistance change of roughly 12% for the 12°F temperature difference seen in Fig.

3(b). This 12% change agrees very well with the results presented in this figure, as the observed difference in stack resistance varies from about 5 to 15%.

The Effect of pH

Figure 8(a) demonstrates that acid addition can have a dramatic effect upon the current efficiency of $CdSO_4$ removal. It is seen that a change of diluate pH (holding other initial stream pH's constant) from 3.2 to 2.3 lowers current efficiencies by 30 to 60%. The reason for this marked decrease in η is that the increased acid concentration allows H^+ ions to carry a significant portion of the current.

Figure 8(b) shows that reducing the pH by approximately one unit reduces the stack resistance by 15 to 50%. The reason for this decrease of resistance is simply that the resistivities of the membranes and solutions have been lowered because of the increased acid concentration.

It can be concluded that pH can be used as an optimization variable since it provides a way of altering current efficiencies and stack resistances. Also, acid addition is often used to prevent precipitation inside of ED stacks (*3*, *19–21*). Therefore, acid addition may be used to lengthen the useful life of ion-exchange membranes and decrease stack resistances, but at the cost of lower current efficiencies.

Membrane Degradation and Fouling

Symptoms of membrane degradation include a decrease in current efficiency and an increase in stack resistance that occur over long-term operation. Scale formation on membrane surfaces can also cause a decrease in membrane performance, but can often be avoided by operating at lower pH values. It is seen from Fig. 9 that none of the above symptoms occurs to any appreciable degree. Any differences present in these current efficiency and stack resistance plots probably fall into the realm of experimental error rather than degradation. Thus, it appears that membrane degradation has not happened after using a set of ion-exchange membranes for more than 100 h in acidic, heavy metal solutions. For practical applications, it may be necessary to monitor η and R_a plots over several thousand hours of operation to determine if membrane degradation is occurring.

Electrode Reactions and Related Phenomenon

For the electrode stream compositions used in this study, the following gases are likely to evolve at the electrodes: H_2, O_2, and Cl_2. Hydrogen gas evolved at the cathode regardless of the anion present in the electrode stream. Chlorine gas was evolved at the anode for systems containing Cl^- as the common ion, as was evidenced by the characteristic odor of chlorine gas and a slight yellowing of the electrode solution. For nonchloride systems, O_2 presumably formed at the anode because there were many bubbles in the electrode solution exiting the stack. Chlorine gas is known to be corrosive to a variety of substances; hence, it is preferable to exclude Cl^- from the anolyte solution if possible. However, such exclusion was not possible for the heavy metal stack because of the membrane configuration and the single electrode stream. Commercial ED units may be able to utilize this Cl_2 as an antibacterial agent for the pretreatment or posttreatment of the diluate stream.

Osmotic Water Transfer

As mentioned earlier, OWT is the water that is transported through ion-exchange membranes as a consequence of the electrodialytic transfer of electrolyte from the diluate to the concentrate. Recall that when temperature and pressure gradients are absent across an ion-exchange membrane, OWT is a function of waters of hydration (or hydration numbers), electroosmosis, and to a lesser degree, normal osmosis. In fact, waters of hydration account for most of OWT (*17*, *38*, *39*). Therefore, OWT is strongly dependent upon the specie of ions being transferred since hydration numbers are specie dependent.

This "specie dependence" of OWT is clearly seen in Fig. 10, where experimental OWT values are plotted for NaCl, $CaCl_2$, $CdSO_4$, and $CdCl_2$. Each experimental OWT point was derived from the net mass and concentration changes that occurred in the diluate over an entire run. Overall there is substantial differentiation between the OWT curves for salts having differing cations (e.g., NaCl vs $CaCl_2$) and lesser differentiation between salts having different anions (e.g., $CdSO_4$ vs $CdCl_2$). Note that the ordinate is in units of liter/mole, i.e., liter(s) of water carried through the membranes per net mole of electrolyte transferred.

When water reuse or concentrate stream minimization (for disposal or electrolyte recovery) is the goal, the ideal scenario for a water/electrolyte reclamation scheme would be to have the OWT as the only water in the concentrate stream. In this case the maximum concentrate concentration would be equal to the electrolyte concentration flowing through the membranes. This is physically represented by the 1/*C* contour (inverse of concentrate concentration) included in Fig. 10. Note that the ordinate has inverse units of the abscissa. The point at which an extrapolated OWT curve intersects the 1/*C* contour corresponds to the maximum concentrate concentration that is obtainable under the operating conditions used in this work. Thus, Fig. 10 indicates that the maximum concentrate electrolyte concentrations for NaCl, $CaCl_2$, $CdSO_4$, and $CdCl_2$ are approximately 2.25, 1.22, 0.95, and 0.87 *M*, respectively. For the concentration ranges studied, average OWT values for NaCl, $CaCl_2$, $CdSO_4$, and $CdCl_2$ are about 0.40, 0.85, 1.08, and 1.12 L/mol, respectively. The above numerical values are membrane specific since OWT depends in part on the average pore size of an ion-exchange membrane (*40*).

The one $CdCl_2$ data point to the right of the 1/*C* contour is from a run that had an initial concentrate concentration that was purposely set above 0.87 *M*. The concentrate stream actually experienced dilution during this run because the solution coming through the membranes from the diluate was less concentrated than the concentrate.

Even though the OWT values of $CdCl_2$ and $CdSO_4$ are the highest of those seen in Fig. 10, they are low enough to provide excellent water reclamation if the average diluate concentations are fairly low (below 0.1 *M*). For example, if the electrolyte concentration of 100 L of 0.01 *M* $CdCl_2$ was reduced by 99%, there would still be about 99 L purified water available for recycle. Table 3 contains approximate percents of water that would be recovered ($\%_{\text{recovered}}$) from $CdCl_2$ diluate solutions at different concentrations.

The maximum concentrate concentrations and average OWT listed above are essentially the same for the adjusted OWT points in Fig. 10. OWT adjustment according to diluate hydration makes little difference in water transfers except for two isolated points in the low concentrate concentration region ($CdCl_2$ and $CdSO_4$ points at ~0.15 *M*). Adjustment of $CaCl_2$ values has little effect since the hydrated diameter of Ca^{2+} ions shows only a small dependence on electrolyte concentration according to Eq. (8).

The hydration model was devised so that a general relationship between hydration numbers at infinite dilution and water transfer could be investigated from a simple theoretical approach. Figure 10 shows that the hydration model exhibits good agreement with experimental OWT points in the cases of $CaCl_2$ and $CdSO_4$, but not for $CdCl_2$. Care should be taken not to infer too much from the good fit the hydration model has with the data. Since this model is based on the experimentally deter-

TABLE 3

$\%_{\text{recovered}}$ for Various $CdCl_2$ Diluate Concentrations[a]

	Final diluate concentration (M)			
Initial diluate concentration (M)	0.1	0.01	0.001	0.0001
0.2	88.8	78.7	77.7	77.6
0.1	—	89.9	88.9	88.8
0.01	—	—	99.0	98.9
0.001	—	—	—	99.9

[a] Note: an average OWT_{CdCl_2} of 1.12 L/mol has been used.

mined OWT values of a reference electrolyte (here, NaCl), there are electroosmosis and normal osmosis contributions included in the m_r and $OWT_{r,C=0}$ terms in Eq. (9). However, since larger multivalent cations may produce greater electroosmotic and normal osmotic contributions than Na^+, the hydration model may tend to underpredict certain osmotic water transfers. This could explain why experimental and theoretical results for $CdCl_2$ showed poor agreement, but does not explain the excellent agreement for $CdSO_4$ results. Perhaps $CdCl_2$ forms more extensive hydrated complexes in solution than $CdSO_4$, resulting in larger OWT values.

Infinite-dilution hydration numbers (h_i^∞) are used in the hydration model in order to keep this model simple by reducing the number of variables to a minimum. The only variable in Eq. (9) is concentrate concentration. The predictive capabilities of this equation could be improved if the hydration numbers were expressed in terms of the diluate concentration (much like d_+ in Eq. 8), but this would add another variable to Eq. (9), increasing the model's complexity.

Many investigators report osmotic water transfers in units of liter/Faraday, where the OWT has been found to decrease with increasing external electrolyte concentration (*15*, *41–43*). However, it is not clear if these investigators are speaking of the diluate or concentrate concentration when they use the term "external concentation." If concentrate concentration is implied, then the OWT curves reported here will agree with the liter/Faraday trend only if the liter/mole transfers are converted into liter/Faraday values by using current efficiencies. Once this conversion is made, the OWT vs concentration curves would have negative slopes, with the possible exception of $CaCl_2$. If the diluate concentration is implied as the external concentration, then no meaningful comparison can be made between the liter/mole values reported here and the liter/Faraday values reported elsewhere. Using liter/mole units for OWT is preferred over liter/Faraday for applications aimed at water reuse or waste minimization.

One explanation for the positive OWT slopes seen in Fig. 10 is as follows. Ions involved in counterion backdiffusion and co-ion intrusion probably carry less water back to the diluate from the concentrate when high concentrate concentrations are present, because ions tend to be less hydrated at higher electrolyte concentrations. Low concentrate concentrations produce less co-ion intrusion and counterion backdiffusion than high concentrate concentrations. Hence, ions that are passing from the diluate to the concentrate would carry more water than the same ions passing from the concentrate to the diluate. As the concentrate concentration increases, η decreases (see Figs. 3 and 4). Since any current inefficiency involves an equal transfer of ions from diluate to concentrate and concentrate to diluate (i.e., current with no net transfer of ions), then the decrease in current efficiency associated with increased concentrate concentrations should result in an increase in water transferred from the diluate to the concentrate. In addition, increased concentration gradients promote greater solvent flux by normal osmosis, which results in overall greater OWT contributions. There is no apparent explanation for the overall negative slope of the $CaCl_2$ curve for OWT expressed in liter/mole.

The NaCl OWT points in Fig. 10 were obtained from runs using 3 V/cell pair (*44*), but 4 V/cell pair was used here for all other electrolyte systems. The literature has clearly shown, for several types of ion-exchange membranes, that the current density dependence of osmotic water transfer decreases substantially as the current density increases (*39–42*), where OWT is virtually independent of the current density for values above 20 mA/cm^2. The average current densities for OWT runs presented in this work are in the range of 20 to 40 mA/cm^2 (even for 3 V/cell pair). Therefore it is assumed that there should be little difference between OWT values obtained at 3 and 4 V/cell pair. Hence, a fair comparison can be made between all of the experimental OWT points given in Fig. 10.

Limiting Current Density and Concentration Polarization

Evidences of concentration polarization were not observed in the experimental runs. The low-level run may be an exception to this, as concentration polarization can have greater effects on current efficiency than co-ion intrusion and counterion backdiffusion when very dilute electrolyte solutions are used (*41*). For the other runs, however, the decrease in η seems to be due to co-ion intrusion and counterion backdiffusion effects. This is supported by two observations. First, precipitation of pH sensitive salts was limited to only a few runs, where a very thin white film was noted on at most two membranes at the conclusion of a run. Second, unusually high resistances and low current efficiencies, which would be caused by concentration polarization over much of the diluate concentration range, are not seen in the results.

Special Application: Removal of Low-Level Cd^{2+}

There are many industrial processes that produce acidic wastewater streams that contain low, yet significant, concentrations of heavy metals. Such streams can be found in electronic manufacturing operations, metal plating operations, as well as certain mining operations. Since many heavy metals are toxic even at low levels in aqueous solutions, they pose a threat to the water quality of aquifers that receive them. Thus, it is often required that heavy metal laden waters be purified before significant amounts of heavy metals can encroach upon aquifers or other such bodies of water. The low-level experiment performed here used a feed (diluate) that had initial cadmium concentration and pH of 31 ppm and 3.8, respectively, whereas the cadmium concentration and pH of the initial concentrate stream was 190 ppm and 3.6, respectively.

The results of the low-level run are contained in Figs. 4 and 5. Figure 4 shows current efficiencies and stack resistances. Figure 5 considers the current efficiencies in greater detail, where it is seen that the current inefficiency due to H^+ removal is relatively small even though the initial diluate had a Cd^{2+} to H^+ ratio of about 2:1. This small H^+ interference may support the notion that concentration polarization has an increased influence in reducing η at low electrolyte concentrations.

Figure 6 shows how the relative diluate and concentrate electrolyte concentrations influence the degree of dilution that is possible for $CdSO_4$ systems. At a given concentrate/diluate ratio, the two curves indicate that the current efficiencies for the low-level run are lower than those for a run employing more concentrated diluate and concentrate streams. This result suggests that concentration polarization has a predominant role in reducing η for the low-level run because the diluate boundary layers next to the membranes are more easily depleted of ions as the bulk diluate electrolyte concentration is decreased.

The low-level results in Fig. 5 show that current efficiencies of at least 50% can be maintained over a tenfold dilution of the diluate. As discussed earlier, osmotic water transfers of low-level electrolyte systems should not limit the water reuse capabilities of ED (see Table 3). Therefore, the limited experimental work done here indicates that it is technologically feasible to use ED to remove heavy metals, present in very low concentrations, from water.

CONCLUSIONS

Cadmium removal exhibited excellent current efficiencies and reasonable stack resistances over a wide range of $CdCl_2$ and $CdSO_4$ concentrations. In general, current efficiencies are shown to decrease as the electrolyte concentration gradient increases between diluate and concentrate compartments. It has been demonstrated that stack resistance is largely a function of the electrolyte concentration in the diluate compartments.

Current efficiencies and stack resistances are somewhat dependent upon the type of electrolyte being removed. Given a diluate and concentrate concentration, current efficiencies tend to increase in the following order: $CdSO_4 < CdCl_2 < NaCl$; whereas stack resistances increase in the order $NaCl < CdCl_2 < CdSO_4$.

An increase in stream temperature and a reduction in diluate stream pH decreases both current efficiencies and stack resistances involved in Cd^{2+} removal. Thus, temperature and pH can be used as optimization variables for ED operations intended for heavy metal removal and/or concentration.

OWT is dependent upon the specie of electrolyte being transferred because it is largely a function of hydration numbers. OWT values measured in this work (liter/mole) generally increase as the concentrate concentration increases. In addition, these water transfers increase in the following order: $NaCl < CaCl_2 < CdSO_4 < CdCl_2$. With the exception of $CdCl_2$, a model based on cation hydration numbers predicts OWT values with good accuracy.

Membrane degradation was not observed for the electrodialytic removal of cadmium salts. Also, except for the removal of heavy metals at very low concentrations (e.g., low-level run), concentration polarization did not appear to be present to any significant extent under the operating conditions used in this work.

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