Kirk-Othmer Encyclopedia of Chemical Technology.

ELECTROSEPARATIONS, ELECTRODIALYSIS

Electrodialysis (ED) is a process for moving ions across a membrane from one solution to another under the influence of a direct electric current (see Dialysis). Classically the process was carried out in three-compartment electrolytic cells in which the compartments were separated from each other by essentially nonselective membranes (see Membrane technology). The end compartments contained electrodes. In 1940, a multicompartment ED process using ion-selective membranes (Fig. 1) was suggested (1) in which membranes *A* selective to anions alternated with membranes *C* selective to cations. When a d-c potential is applied, cations M^+ tend to move toward the negatively charged cathode. These ions are able to permeate the cation-selective membranes but not the anion-selective membranes if the latter are perfectly selective. Similarly, anions X^- tend to move toward the positively charged anode. These ions are able to permeate the anion-selective membranes but not the cation-selective ones. As a result, the odd-numbered compartments in the figure become depleted in electrolyte, the even-numbered compartments enriched.

1. Membranes

In 1950, ion-selective membranes having high selectivity, low electrical resistance, good mechanical strength, and good chemical stability were described (2). These were essentially insoluble, synthetic, polymeric, organic ion-exchange (IX) resins in sheet form (see Ion exchange). Typical chemical structures for modern membranes of this type are shown schematically in Figure 2. The cation-selective membranes (Fig. 2**a**) consist of cation-exchange (CX) resin composed of polystyrene having negatively charged sulfonate groups chemically bonded to most of its phenyl groups. The charges of the sulfonate groups are electrically balanced by positively charged cations (counterions). Sulfonated polystyrene swells greatly in water. The amount of swelling is typically controlled by including cross-linking agents in the polymer, represented by divinylbenzene in Figure 2; by incorporating electrically neutral polymers; or by having extensive regions (blocks) in the polymer which lead to substantial microcrystallinity. The positively charged counterions, eg, Na^+, Ca^{2+}, or Mg^{2+}, are appreciably dissociated from the chemically bound negatively charged groups once the membrane is exposed to water. Thus, in water, the counterions are mobile, and may be exchanged for other cations from an ambient solution, maintaining the electrical neutrality of the membrane. This high (typically > 1 meq/cm^3 of membrane) concentration of counterions in IX resins is responsible for the low electrical resistance of the membrane. The high concentration of bound negatively charged groups tends to exclude mobile negatively charged ions (co-ions) from an ambient solution and is responsible for the high ion selectivity of the membranes.

The anion-selective (AX) membranes (Fig. 2**b**) also consist of cross-linked polystyrene but have positively charged quaternary ammonium groups chemically bonded to most of the phenyl groups in the polystyrene instead of the negatively charged sulfonates. In this case the counterions are negatively charged, eg, Cl^-, $HCO^-{}_3$, $NO^-{}_3$, or $SO^{2-}{}_4$.

Commercially available membranes are usually reinforced with woven, synthetic fabrics to improve the mechanical properties. Several hundred thousand square meters of IX membranes are now produced annually,

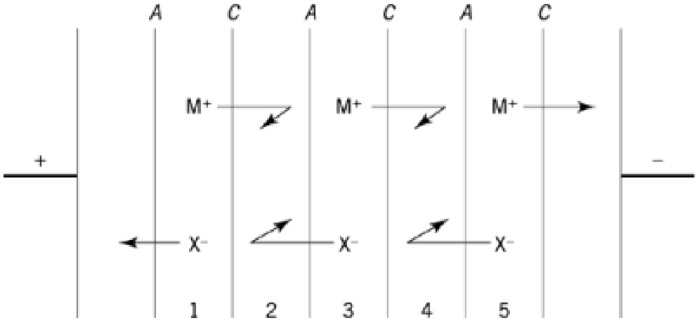

Fig. 1. Principle of multicompartment electrodialysis. See text.

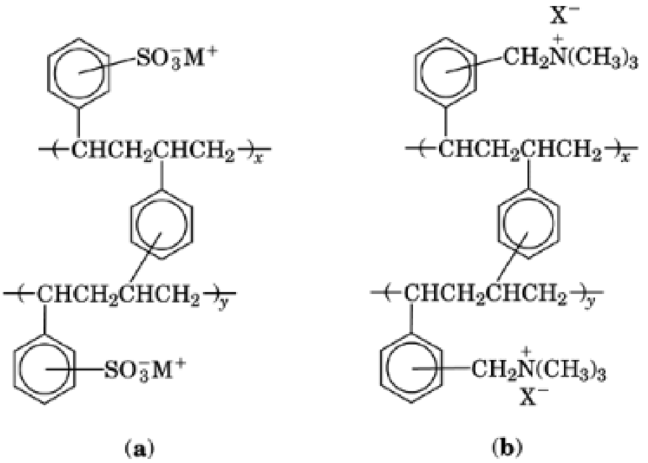

Fig. 2. Schematic representation of (**a**) cation-exchange resin, and (**b**), anion-exchange resin.

and the mechanical and electrochemical properties are varied by the manufacturers to suit the proposed applications. The electrochemical properties of most importance for ED are (*1*) the electrical resistance per unit area of membrane; (*2*) the ion transport number, related to current efficiency; (*3*) the electrical water transport, related to process efficiency; and (*4*) the back-diffusion, also related to process efficiency.

Commercial IX membranes have thicknesses of ca 0.15–0.5 mm and electrical resistances of ca $3 - 20\ \Omega\cdot\text{cm}^2$ at 25°C when in equilibrium with 0.5 N sodium chloride. The electrical resistances are somewhat higher in more dilute solutions because co-ions are more effectively excluded from the membrane by the IX resin. The electrical resistance decreases with increasing temperature at a rate of ca $-1.9\%/^\circ$C. The electrical resistance of an ED apparatus depends in large part on the electrical resistances of the membranes when electrolyte solutions are in excess of about 0.1 N. For more dilute solutions the resistance of the apparatus tends to be dominated by the resistance of the solution being demineralized.

The ion transport number is defined as the fraction of current carried through the membrane by counterions. If the concentration of fixed charges in the membrane is high compared to the concentration of the ambient solution, then the mobile ions in the IX membrane are mostly counterions, co-ions are effectively excluded, and the ion transport number then approaches 1. Commercial membranes have ion transport numbers in dilute solutions of ca 0.85–0.95. The relationship between ion transport number and current efficiency is shown in Figure 3 where $\bar{t}_{-}^{A}$ is the fraction of current carried by the counterions (anions) through the AX membrane and

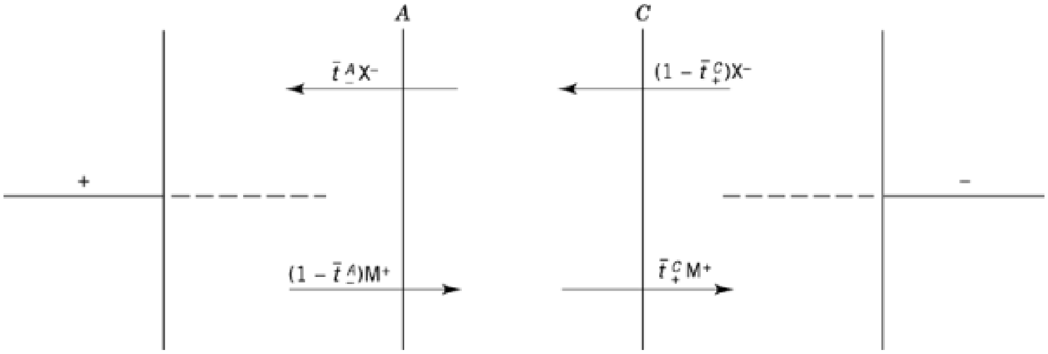

Fig. 3. Relationship between current efficiency and ion transport number.

$\bar{t}_+^C$ is the fraction of current carried by the counterions (cations) through the CX membrane. The remainder of the current $(1 - \bar{t}_-^A) = \bar{t}_+^A$ in the case of the AX membranes and $(1 - \bar{t}_+^C) = \bar{t}_-^C$ in the case of the CX membranes is carried by co-ions and constitutes an electrical inefficiency. The net transport of electrolyte is then given by:

$$\bar{t}_-^A - \left(1 - \bar{t}_+^C\right) = \bar{t}^{A-} - \bar{t}_-^C = \bar{t}_+^C - \bar{t}_+^A$$

. The electrical water transport is defined as water that accompanies the electrical transport of ions through the membranes. Owing to the high concentration of counterions in IX membranes, the transport of ions and water are closely coupled, ie, the internal solution tends to move in piston-like flow. The electrical water transport is ca 100–200 cm^3/eq of ions transferred. This value is toward the low end of the range for AX membranes and toward the high end for CX membranes. In the case of dilute solutions, water transport is not of significant engineering importance. However, in more concentrated solutions, such as seawater, the water transport can be a significant fraction of the volume of solution electrodialyzed and, therefore, constitutes a process inefficiency. Generally, membranes having low water contents and high concentrations of fixed, charged groups have low electrical water transport. Such membranes also tend to have high ion transport numbers and are therefore preferred for concentrated electrolytes.

Back-diffusion is the transport of co-ions, and an equivalent number of counterions, under the influence of the concentration gradients developed between enriched and depleted compartments during ED. Such back-diffusion counteracts the electrical transport of ions and hence causes a decrease in process efficiency. Back-diffusion depends on the concentration difference across the membrane and the selectivity of the membrane; the greater the concentration difference and the lower the selectivity, the greater the back-diffusion. Designers of ED apparatus, therefore, try to minimize concentration differences across membranes and utilize highly selective membranes. Back-diffusion between sodium chloride solutions of zero and one normal is generally $<$ca 2×10^{-6} meq/(s·cm^2).

1.1. Bipolar ED

Bipolar ED membranes have one surface consisting of CX resin and the opposite surface of AX resin. When a direct current is passed through such a membrane in a direction to pull anions out of the interface between the AX and CX resins and through the AX resin, the interface rapidly becomes depleted of all ions other than those resulting from the dissociation of water. Dilute alkali can therefore be produced at the outer surface of the AX region and dilute acid at the outer surface of the CX layer (3). An enormous effort has been applied by the AquaTech division of Allied-Signal Corp. to refine and commercialize this technology, which as of this writing is without signal commercial success.

The bipolar membranes are used in a more or less conventional ED stack together with conventional unipolar membranes. Such a stack has many acid–alkali producing membranes between a single pair of end electrodes. The advantages of the process compared to direct electrolysis seem to be that because only end electrodes are required, the cost of the electrodes used in direct electrolysis is avoided, and the energy consumption at such electrodes is also avoided.

The disadvantages appear to be that the bipolar membranes are comparatively expensive, and the economic life is limited to about one year. Such short lifetime appears to result from the very high $(\sim 10^6\ \mathrm{V/cm})$ voltage gradients at the interface between the AX and CX regions. Additionally, practical current densities are limited to about 1000 A/m^2 available area.

2. Apparatus

The apparatus for ED is fundamentally an array of alternating AX and CX membranes terminated by electrodes. The membranes are separated from each other by gaskets which form fluid compartments. Compartments that have AX membranes on the side facing the positively charged anode are electrolyte-depletion compartments. These are also called demineralizing, diluting, diluate, or dilute compartments. The remaining compartments are electrolyte-enrichment compartments, also called concentrating, concentrate, or brine compartments. The enrichment and depletion compartments also alternate through the array. Holes in the gaskets and membranes register with each other to provide two pairs of internal hydraulic manifolds to carry fluid into and out of the compartments. One pair communicates with the depletion compartments, and the other with the enrichment compartments. Much effort has been expended on the design of the entrance and exit channels from the manifolds to the compartments to prevent unwanted cross-leak of fluid intended for one class of compartment into the other class. This effort has been made increasingly difficult by the trend to thinner membranes and gaskets, the latter determining membrane spacing and the thickness of the fluid compartments; such trends are intended to reduce energy consumption. A contiguous group of two membranes and the associated two fluid compartments is called a cell pair. A group of cell pairs and the associated end electrodes is called a stack or a pack. Generally 100–600 cell pairs are arranged in a single stack, the choice being made on the basis of ED capacity desired, the uniformity of flow distribution achieved among the several compartments of the same class in a stack, and the maximum total direct current potential desired. One or more stacks may be arranged in a press, designed to compress the membranes and gaskets against the force of fluid flowing through the compartments thereby preventing fluid leaks to the outside and internal cross-leaks between compartments. For small presses such compression is usually provided by tierods; for larger presses hydraulic rams are frequently used.

Commercial membranes have typical thicknesses of ca 0.15–0.5 mm; the compartments between the membranes have typical thicknesses of ca 0.5–2 mm. The thickness of a cell pair is therefore in the 1.3–5.0 mm range, commonly about 3.0 mm. One hundred cell pairs have a combined thickness of about 300 mm. The effective area of a cell pair for current conduction is generally on the order of 0.2–2 m^2.

In concentrated electrolytes the electric current applied to a stack is limited by economic considerations, the higher the current I the greater the power consumption W in accordance with the equation $W = I^2 R_s$, where R_s is the electrical resistance of the stack. In relatively dilute electrolytes the electric current that can be applied is limited by the ability of ions to diffuse to the membranes. This is illustrated in Figure 4 for the case of an AX membrane. When a direct current is passed, a fraction $(t_-^A \simeq 0.85 - 0.95)$ is carried by anions passing out of the membrane–solution interface region and through the membrane. In the bulk solution, a fraction t_- of the current is carried by anions passing into the interfacial region. Generally t_- is significantly less than $\bar{t}_-^A$. For example, in the case of sodium chloride, t_- is ca 0.6. As the electric current continues to pass, the interfacial region becomes depleted in electrolyte. The difference between the quantity of anions transferred out of the interfacial region and those transferred in must be made up by convection and diffusion. If the interfacial region is defined as the region of streamline flow, then diffusion is the only mechanism, other than conduction, available to bring anions into the region. At steady state the concentration of electrolyte in the solution at the membrane surface must be reduced sufficiently from the bulk value to provide the concentration gradient necessary to bring in by diffusion the difference between the anions carried out of and into the interfacial regions by the electric current. This may be expressed by:

$$i\bar{t}_-^A = it_- + FD\left(c_b - c\right)/\delta$$

where F is Faraday's constant 96,500 C, the quantity of electric current required to transfer one equivalent of ions through a perfectly selective membrane; i is the current density in A/cm^2; D is the diffusion constant for the electrolyte, cm^2/s; c_b, is the concentration of the electrolyte in the bulk (nonstreamline region), g·eq/mL; c, also in g·eq/mL, is the concentration of electrolyte in solution at the membrane surface; and δ in cm is the thickness of the interfacial (streamline flow) region. This expression may be rearranged to:

$$i = \frac{DF\left(c_b - c\right)}{\delta\left(\bar{t}_- - T_-\right)}$$

Hence in any given situation the maximum current density that can be carried by a combination of electrical conduction and diffusion occurs when c, the concentration in the solution at the membrane surface, approaches zero, ie,

$$i_{\max} = \frac{FDc_b}{\delta\left(\bar{t}_-^A - t_-\right)}$$

For a typical electrodialysis apparatus, δ appears to be of the order of 5×10^{-3} cm, and $\bar{t}_-^A$ is about 0.9. For dilute sodium chloride solutions, D is ca1.5×10^{-5} cm^2/s and t_- about 0.6. Under these circumstances the ratio $i_{\max}/c_b$, is ca 1000 A·cm/(g·eq), ie, $i_{\max}$ is ca 0.1 A/cm^2 when c_b is ca 0.1 N. Increasing temperature increases D by ca 2.3%/°C, and decreasing δ increases $i_{\max}$. Therefore, designers usually include some kind of structure in the ED compartments to break up the streamline interfacial region and bring electrolyte as close as possible to the membrane surface by convection. The maximum current also increases as the difference $(\bar{t}_-^A - t_-)$ decreases. As $\bar{t}_-^A$ approaches t_-, the diffusion-controlled limitation on current density vanishes and the current density may be increased without limit. However, power consumption increases as i^2R and puts an economic limitation on current density. When $\bar{t}_-^A$ approaches t_-, the anion membrane loses its selectivity and becomes essentially neutral. The net transport of electrolyte is then given by $(t_- - \bar{t}_-^C)$. Thus for many electrolytes, an ED apparatus utilizing alternating neutral and CX membranes exhibits substantial depletion and enrichment (4). For example, in the case of sodium chloride solutions the net transport of electrolyte is 0.8 (current efficiency, 80%) when the ion transport numbers of the AX and CX membranes are each 0.9. If the AX membrane is replaced by a neutral membrane, the net transport is 0.5 (current efficiency, 50%) when the concentration difference between enriched and depleted compartments is small. ED apparatus using neutral membranes has not been commercially successful.

2.1. Polarization

When the applied current density equals $i_{\max}$, the AX membrane and the apparatus are said to be concentration polarized or simply polarized. At $i_{\max}$ the fluid at the surface of the membrane is essentially depleted of electrolyte and the electrical resistance of the apparatus increases substantially even though the bulk solution in the depletion compartments may still contain an appreciable concentration of electrolyte. This is a sign of polarization.

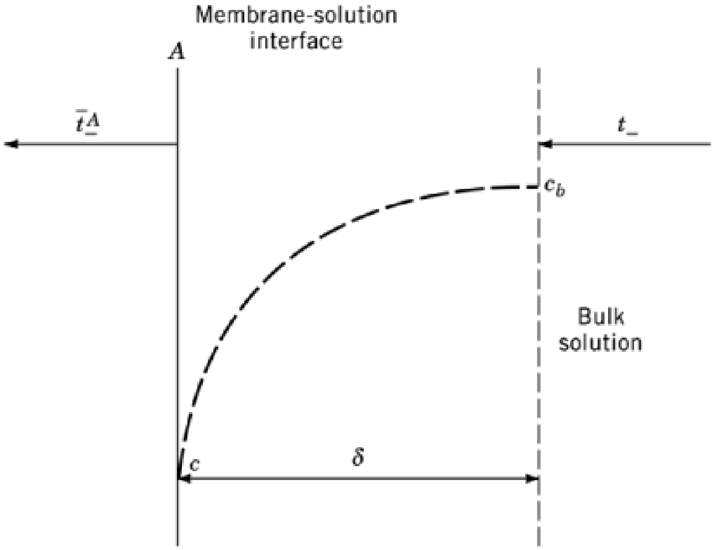

Fig. 4. Current limitation controlled by diffusion to anion membrane.

At the polarization current density, ions resulting from the dissociation of water have concentrations comparable to the concentration of electrolyte at the surface of the membrane. A significant fraction of the current through the AX membrane is then carried by hydroxide ions into the enrichment compartments. Hydrogen ions are carried into the bulk solution in the depletion compartments. Changes in the pH of the enrichment and depletion compartments are another sign of polarization.

If $i_{\max}$ is substantially exceeded, electrolytes that are insoluble at high pHs, such as calcium carbonate and magnesium hydroxide, may precipitate at the interface between the AX membrane and the enriched solution. This is a third sign of polarization.

In sodium chloride solutions the ion transport number for Na^+ is about 0.4 compared to about 0.6 for Cl^-. Thus a CX membrane would be expected to polarize at lower current densities than an AX membrane. Careful measurements show that CX membranes do polarize at lower current densities; however, the effects on pH are not as significant as those found when AX membranes polarize. Such differences in behavior have been satisfactorily explained as resulting from catalysis of water dissociation by weakly basic groups in the AX membrane surfaces and/or by weakly acidic organic compounds absorbed on such surfaces (5).

Many fluids of natural origin contain detectable quantities of high molecular weight organic anions, such as those from humic, fulvic, and tannic acids, which can be carried to and deposited on AX membranes. Such deposits can behave as thin films partially selective to cations (6). The interfaces between such films and the underlying AX membranes then act as very thin stagnant depletion compartments and the AX membranes may exhibit polarization at current densities that are much lower than would be expected for new membranes in the absence of such anions.

2.2. Performance

The performance of an ED stack may be estimated by considering the material balance around the stack:

$$\Delta (vc) = v_i c_i - v_o c_o = \frac{\bar{i} E A_p N_p}{F}$$

where v_i and v_o are the flow rates in mL/s into and out of the depletion compartments of the stack, respectively; c_i and c_o are the concentrations in g·eq/mL into and out of the depletion compartments, respectively; $\bar{\imath}$ is the average current density in A/cm^2; E is the net ion transfer ($\bar{t}_-^A - \bar{t}_-^C$); A_p is the current-carrying area per cell pair, cm^2; N_p is the number of cell pairs in the stack; and F is Faraday's constant. Typically a stack is designed so that $v_o c_o$ is ca 50% of $v_i c_i$. This is because $\bar{\imath}_{\max}$ is determined by c_o. When c_o is very small compared to c_i, then $\bar{\imath}$ may be uneconomically low. As a matter of conservative engineering practice, the stack is designed so that $\bar{\imath}$ is appreciably lower than $\bar{\imath}_{\max}$.

The power consumption W may be estimated from $\bar{\imath}^2 R_p A_p N_p$ where R_p, the electrical resistance of a cell pair per unit area ($\Omega\cdot\text{cm}^2$), is given by:

$$R_p = R_d + R_e + R_C + R_A + R_{df} + R_T$$

R_d is the average resistance of a depletion compartment; R_e is the average resistance of an enrichment compartment; R_C is the average resistance of the CX membranes; R_A is the average resistance of the AX membranes; R_{df} is the resistance contributed by depletion in the membrane-solution interfaces; and R_T is the resistance offered by the concentration potential between the enrichment and depletion compartments, ie, a measure of the thermodynamic work required to achieve the concentration difference.

Generally these individual contributions to R_p are not separately measured or calculated. Instead R_p itself is correlated with $\bar{\imath}$, c_o and c_i. For dilute solutions (7):

$$R_p = b + \frac{a}{c_a}$$

where a and b are empirically determined constants and c_a is the average concentration defined as:

$$c_a = \frac{2c_{le}c_{ld}}{c_{le} + c_{ld}}$$

The subscripts have the following significance: *ld* indicates the log-mean concentration in the depletion compartments; *le* indicates the log-mean concentration in the enrichment compartments.

Typical values at room temperature are a, $0.001 - 0.0025\ \Omega\cdot\text{g}\cdot\text{eq/cm}$; b, ca $20 - 40\ \Omega\cdot\text{cm}^2$. The values of a and b within the ranges depend on electrolyte composition and on design of the electrodialysis apparatus. As stated above, R_p decreases with increasing temperature at ca $-1.9\%/^\circ\text{C}$. Typical d-c voltages are ca 0.5–1 volt per cell pair. Assuming an overall current efficiency of 90% this implies a d-c electrical energy requirement of ca $15 - 30$ W·h/g·eq of electrolyte transferred. To this must be added the energy consumption of auxiliary equipment such as pumps and instrumentation, about 500 W·h/m^3, and energy losses during conversion of ac to dc. In the case of relatively concentrated electrolytes, for economic reasons, designers tend to choose d-c voltages per cell pair from the low end of the range mentioned above.

3. Uses

3.1. High Purity Water

Electrodialysis is being increasingly used in conjunction with other processes to produce pure and ultrapure water for use in high pressure boilers and in electronics and pharmaceutical manufacture (8, 9). A typical application minimally involves six steps: (*1*) potable or brackish water is treated via cross-flow ultrafiltration (UF) (see Ultrafiltration) to remove particulate matter; (*2*) the water is treated by reversing-type electrodialysis (EDR) to remove about 90% of the electrolytes; (*3*) the product of electrodialysis is then subjected to reverse osmosis (qv) to remove a substantial fraction of silica and organics, and about 90% of the remaining electrolytes;

(*4*) the permeate from reverse osmosis is further demineralized by electrodeionization (EDI) to remove a further 90 to 95% of the electrolytes still remaining; (*5*) the water is finally treated by mixed-bed ion-exchange deionization followed by (*6*) microfiltration. Activated carbon may be included to remove organic materials. Chlorine, chlorine dioxide, ozone, hydrogen peroxide, and/or uv irradiation may be used to sterilize the water and/or partially oxidize the organics to enable the latter to be more easily removed.

In any given hybrid process train designed for the production of ultrapure water, any one or more of the process steps may be omitted. These trains have very low chemical and operator requirements. By utilizing EDR, which has almost no requirement for chemical additives or chemical cleaning, before reverse osmosis, the requirement of the latter for chemical additives is essentially eliminated. Usage of EDI reduces the need for chemical regeneration of mixed-bed ion-exchange deionizers by about a factor of 10 to 20. These deionizers are nevertheless needed to produce ultrapure water of the highest possible electrical resistivity.

3.2. Brackish Water

Production of potable water from brackish water has been one of the principal applications of ED (see Water supply and desalination). The term brackish water is used to define a water that is more saline than potable water but appreciably less so than seawater. Brackish waters readily available worldwide have concentrations of electrolyte of ca 20–200 meq/L. Potable water generally has <10 meq/L and seawater ca 600 meq/L. A typical application would be demineralization from 0.05 to 0.005 N for which, at one volt per cell pair, d-c energy consumption would be expected to be ca 1.35 kWh/m^3 of potable water. Auxiliaries would add about $0.50\ kW{\cdot}h/m^3$. The specific production rates are ca 0.5 $m^3/m^2{\cdot}d$ of effective cell pair area. In 1993 the installed cost was about $135 per m^2 for large plants, including the immediate electrodialysis auxiliaries such as a-c/d-c conversion equipment, pumps, and instrumentation, but not including the costs of land, buildings, brackish water collection and pretreatment, and potable water storage and distribution. Pretreatment generally consists of filtration to remove suspended particulate matter. Small plants may cost from two to four times as much per square meter.

Direct current enters an ED stack at one end through a positively charged anode, generally a refractory metal such as titanium, coated with a thin film of a noble metal or noble metal oxide (see Metal anodes). The transition from an electron current in the anode to an ionic current in electrolyte bathing the anode produces hydrogen ions and oxygen from the salts in the brackish water. Because hundreds of cell pairs are usually used in an ED stack, the number of equivalents of hydrogen ions and oxygen is generally $<1\%$ of the number of equivalents of electrolyte removed by the membranes. The anodes are usually flushed with some of the brackish water to carry away the anode products. The electric current leaves the stack at the other end through a negatively charged cathode generally also titanium coated with noble metal or noble metal oxide. At the cathode, the electric current produces hydrogen gas and hydroxide ions, again in very small quantities compared to the amount of electrolyte removed through the membranes. However, the hydroxide ions can cause precipitation of calcium carbonate or magnesium hydroxide, or both, resulting from the Ca^{2+} or Mg^{2+} ions in the brackish water.

In some ED plants, strong mineral acids, such as sulfuric or hydrochloric, are added to the brackish water which flushes the cathodes. These acids prevent precipitation but are an additional cost and an inconvenience particularly for small plants.

By using reversing-type or EDR stacks, in which each electrode is alternately anodic and cathodic (10), acid need not be added to the cathode. After passing current through the stack for a period of from about 15 minutes to 24 hours the direction of electric current is reversed for a similar period; that is the electrode that was cathodic in the first half of the cycle and precipitated some alkali-insoluble salts, becomes anodic in the second half. Hydrogen ions generated during the anodic half of the cycle dissolve and separate insoluble salts from the electrode. In the EDR stack, compartments that were enriching during one half of the cycle are depleting during the other half. Appropriately placed automatic valves interchange the entering and exiting fluid streams at the beginning of each half cycle. Several thousand EDR plants have been successfully operated for many years. The periodic reversal also removes foreign substances from the EDR stack per se. Such materials may include alkali-insoluble salts such as calcium carbonate produced by marginal concentration polarization at the interfaces between the depleting fluid and the AX membranes; poorly soluble salts, such as calcium sulfate, which precipitate if the solubility limits are exceeded in the enrichment compartments; and high molecular weight organic anions such as humic and fulvic acids which, if present, may tend to be absorbed on AX membranes.

The success of EDR in water demineralization has apparently resulted from its greater tolerance of particulate and fouling matter compared to reverse osmosis; greater forgivingness of process upsets; greater tolerance for unskilled operators; simplicity in design and construction of EDR stacks compared to reverse osmosis modules; the ability to inspect, clean, or replace one membrane at a time; the existence of a comprehensive global sales and service network; and a vertically integrated manufacture. The economic life of IX membranes in the demineralization of water is generally in excess of 10 years in well-operated plants.

Trends in ED appear to be reduction in pumping and direct ED energy, increase in electric current density, and the use of EDR and hybrid processes in plants in which the manufacturer of the demineralization plant owns and operates the plant, selling water to the user or water distributor.

3.3. Concentration of Seawater by ED

In terms of membrane area, concentration of seawater is the second largest use. Warm seawater is concentrated by ED to 18 to 20% dissolved solids using membranes with monovalent-ion-selective skins. The EDR process is not used. The osmotic pressure difference between about 19% NaCl solution and partially depleted seawater is about 20,000 kPa (200 atm) at 25°C, which is well beyond the range of reverse osmosis. Salt is produced from the brine by evaporation and crystallization at seven plants in Japan and one each in South Korea, Taiwan, and Kuwait. A second plant is soon to be built in South Korea. None of the plants are justified on economic grounds compared to imported solar or mined salt.

3.4. Industrial Wastes

Closely related to seawater concentration is the simultaneous concentration of industrial effluents and recycle of recovered water (see Wastes, Industrial). These applications are expected to increase as environmental restrictions increase. Examples are the concentration of blowdown from cooling towers in power plants; concentration of reverse osmosis blowdown; and the processing of metal treatment wastes (11) (see Metal treatments).

3.5. Electrodeionization

Electrodeionization (EDI) (12) was developed in the 1960s (13) and has been pursued more recently (14). At least the demineralization compartments of ED apparatus are filled with AX and/or CX beads or fibers or the IX membranes are embossed and in contact with each other. In the reversing type of EDI, both compartments are so filled. At low current densities the filling acts to augment the surface area of the membranes resulting in a very large increase in allowable current density. At high current densities water splitting occurs, as in the case of normal ED, and the IX filling is converted largely to the hydroxide and hydrogen forms, respectively. The apparatus is then essentially IX regenerated in real time electrochemically.

The EDI process has begun to find commercial applications, almost always as part of a hybrid process for producing demineralized water (8). When essentially 18 MΩ water is required, EDI reduces the load on mixed-bed IX by an order of magnitude or more. The need for regeneration and regeneration chemicals is reduced by about the same factor. Applications are for feed water for high pressure boilers and for ultrapure water for the electronics industry. When less than 18 MΩ water is satisfactory, EDI can entirely replace mixed-bed IX.

Typically EDI is preceded in a hybrid plant by some combination of EDR, RO, UF or MF, IX water softening and/or absorbent for organics. The tendency of demineralized water producers to reduce chemical requirements seems to assure a future for EDI.

3.6. Miscellaneous Applications

The largest miscellaneous application of ED is the demineralization of whey and nonfat milk for food and feed applications (see Dairy substitutes; Feeds and feed additives; Milk and milk products). During the manufacture of cheese or of milk casein a serum is often produced which contains much of the albumin, globulin, lactose, and minerals present in the milk plus acid and/or salt added during manufacture. The albumin and globulin are a valuable food or feed sources but use is generally limited by the electrolytes present. Since the 1960s, ED and EDR have been used to remove excessive electrolytes, generally from concentrated serum. There are approximately 70 such ED or EDR plants worldwide having about 35,000 m^2 total installed membrane area and producing about 150,000 t/yr of demineralized whey solids. Some plants remove in excess of 90% of the ash content of whey. Others remove only roughly 50% of such ash, the remainder being removed by strong acid cation exchange followed by weak base anion exchange. Much of the highly demineralized product is used as a component of mothers' milk replacement.

Other applications include (*1*) recovery of valuable components from metal plating or treating effluents, including the recovery of hydrofluoric and nitric acids by bipolar ED from stainless steel spent pickle liquor (see Electroplating; Metal surface treatments); (*2*) deashing of beet, cane, or other sugar (qv) juices and molasses. AX membranes are generally subject to fouling by medium molecular weight organic carboxylic acids in such solutions. Although fouling resistant AX membranes have been proposed, the generally short processing season for such sugar solutions leads to high capital charges. Further the additional sugar which could be recovered through desalting is not justified in view of the agricultural policies of the sugar producing countries. There are few, if any, ED plants desalting sugar solutions; (*3*) deacidification/acidification of fruit juices (qv). There are a few plants on a commercial scale; (*4*) desalting of soy sauce, amino acid solutions, fermentation (qv) products, etc (see Amino acids). There are a few small ED plants in such applications; and (*5*) demineralization of blood plasma (see Fractionation, Blood-plasma fractionation). There are few such plants.

4. Economic Aspects

The first commercial ED apparatus was sold in 1954 and installed in Saudi Arabia for desalting brackish water. Since then more than 5000 ED plants have been installed worldwide for the demineralization of brackish and potable water. These range in capacity from a few to more than 10,000 m^3/d.

Ionics Incorporated (Watertown, Massachusetts), the leading ED supplier, has sold more than 2000 ED and EDR plants having a combined capacity of probably more than 600,000 m^3/d. These were originally furnished with probably more than 1.2×10^6 m^2 of membrane. More than 2000 other ED and EDR plants have been built and installed in China. These plants have a combined capacity of more than 600,000 m^3/d and were originally furnished with probably more than 1.2×10^6 m^2 of membrane. Also it is estimated that more than 1000 ED and EDR plants have been built and installed in the CIS. These plants have a combined capacity of probably more than 300,000 m^3/d, probably originally furnished with more than 600,000 m^2 of membrane. Roughly 100 plants have been installed by other companies such as Corning France (formerly S.R.T.I.) and Portals Water Treatment Ltd. (formerly Permutit-Boby).

4.1. Nomenclature

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a = empirically determined constant representing that portion of cell pair resistance that is inversely proportional to the average concentration in the cell pair, $\mathrm{ohm{\cdot}eq/cm}$
A_p = current carrying area per membrane, cm^2
b = empirically determined constant representing that portion of cell pair resistance that is independent of the average concentration in the cell pair, $\mathrm{ohm{\cdot}cm^2}$
c = concentration, eq/mL
c_a = average concentration in the cell pair, eq/mL, harmonic mean
c_b = bulk concentration at any point in a depletion cell, eq/mL
c_i = concentration of solution inlet to depletion compartment, eq/mL
c_ld = log-mean concentration in depletion compartment, eq/mL
c_le = log-mean concentration in enrichment compartment, eq/mL
c_o = concentration of solution from the outlet of a depletion compartment, eq/mL
D = diffusion constant of an electrolyte, cm^2/s
E = net ion transfer or transport, dimensionless
F = Faraday's constant, about 96,500 C/$\mathrm{gram{\cdot}eq}$
i = current density, $\mathrm{A/cm}^2$
$\bar{i}$ = average current density, $\mathrm{A/cm}^2$
I = current, A
N_p = number of cell pairs in a stack, dimensionless
R_A = average areal resistance of AX membrane, $\mathrm{ohm{\cdot}cm^2}$
R_C = average areal resistance of CX membrane, $\mathrm{ohm{\cdot}cm^2}$
R_d = average areal resistance of depletion compartment, $\mathrm{ohm{\cdot}cm^2}$
R_df = average areal resistance contributed by depletion in the membrane-solution interfaces, $\mathrm{ohm{\cdot}cm^2}$
R_p = average areal resistance of cell pair, $\mathrm{ohm{\cdot}cm^2}$
R_s = electrical resistance of stack, ohms
R_T = average areal resistance offered by the concentration potential between the enrichment and depletion compartments, $\mathrm{ohm{\cdot}cm^2}$
t_- = fraction of current carried by anions in the bulk solution in the depletion compartment, dimensionless
$\bar{t}_+^A$ = fraction of current carried through an AX membrane by cations (co-ions), dimensionless
$\bar{t}_-^A$ = fraction of current carried through an AX membrane by anions (counterions), dimensionless
$\bar{t}_+^C$ = fraction of current carried through CX membrane by cations (counterions), dimensionless
$\bar{t}_-^C$ = fraction of current carried through CX membrane by anions (co-ions), dimensionless
v = volumetric flow rate of solution, mL/s
v_i = volumetric flow rate of solution entering a compartment, mL/s
v_o = volumetric flow rate of solution out of a compartment, mL/s
δ = thickness of interfacial, streamline flow region, cm

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