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ELECTRODIALYSIS AND ITS APPLICATION IN THE CHEMICAL PROCESS INDUSTRY

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I. Introduction

Electrodialysis is a process by which electrically charged membranes are used to separate ions from an aqueous solution by the driving force of an electrical potential difference. Electrodialysis is used today mainly for desalination of sea and brackish water. Other applications, such as the recovery of water and valuble metal ions from industrial effluents, the removal of salts and acids from pharmaceutical solutions and in food processing, have only recently generated a broader interest. Electrodialysis is used today to perform several general types of separations:

- The removal of salts, acids, and bases from aqueous solutions
- The separation of ionic compounds from neutral molecules
- The separation of monovalent ions from multivalent ions.

In addition to these separation procedures electrodialysis is used in combination with bipolar membranes for the production of acids and bases from waste water containing salts. These more recently developed applications of electrodialysis have substantially increased the interest in this process for the chemical, food and drug industry.

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II. The Principle of Electrodialysis and Basic Process Parameters

Electrodialysis is based on the selective electromigration of ions through cation- and anion-exchange membranes. Cation-exchange membranes are negatively charged and permit the passage of positively charged cations which are generally referred to as counter-ions. Anion-exchange membranes are positively charged and permit the passage of negatively charged anions. Ion-exchange membranes are, due to the Donnan exclusion,1) more or less completely impermeable to ions carrying the same charge as the membranes. These ions are generally referred to as co-ions. The basic principle of the process is illustrated in Figure 1 which shows a schematic diagram of a typical electrodialysis cell arrangement consisting of a series of anion- and cation-exchange membranes in alternating patterns between an anode and a cathode to form individual cells.

If an ionic solution, such as an aqueous salt solution, is pumped through these cells and a direct current potential is applied between the electrodes the positively charged cations in the solution migrate towards the cathode. These ions pass easily through the negatively charged cation-

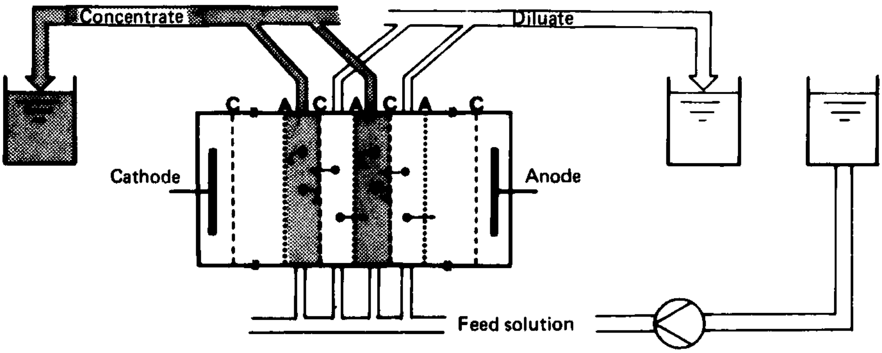


FIGURE 1

The principle of electrodialysis showing the migration of cations and anions through the corresponding membranes under the driving force of an electrical potential difference resulting in a concentration decrease or increase, respectively, in alternating cells.

exchange membranes but are retained by the positively charged anion-exchange membranes. Likewise, the negatively charged anions in the solution migrate towards the anode. They pass through the anion-exchange membrane but are retained by the cation-exchange membranes. The overall result is an ionic concentration increase in alternate compartments while the other compartments simultaneously become depleted of ions. The depleted solution is generally referred to as diluate and the concentrated solution as concentrate or brine.

1. The electrodialysis stack design

In a practical electrodialysis system up to 400 cation- and anion-exchange membranes are installed in parallel to form an electrodialysis stack with up to 200 cell pairs. There are several different electrodialysis stack designs in commercial use. They typically are patterned after the plate and frame configuration utilized in filter presses. A typical stack design is shown in Figure 2.

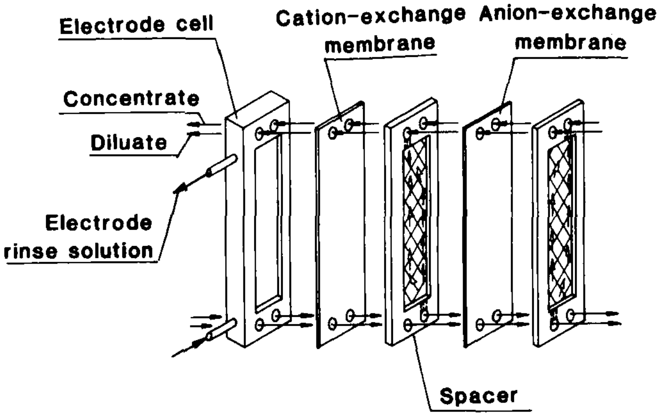


FIGURE 2

Schematic diagram of an electrodialysis stack showing the feed flow distribution in cells formed by the ion-exchange membrane and spacer gaskets.

Cation- and anion-exchange membranes separated by a spacer gasket form individual cells. Common holes through the membranes and separator gaskets act as flow manifolds. The flow distribution to the individual compartments is accomplished by using special ducts from the entry and the exit holes to the interior of the spacer gasket. Electrodes are placed at the ends of a membrane stack in individual cells, usually referred to as electrode chambers. Various materials are used for the fabrication of the electrodes. Usually a platinium coated titanium screen is used as the anode because of the high level of corrosion resistance. The cathode is generally made from nickel alloys or stainless steel. The electrode chambers are rinsed by a separate solution which is free of chloride-ions to avoid the formation of highly corrosive chlorine gas. The thickness of the individual cells, i. e., the distance between two membranes is kept as small as possible, usually in the range of 1 mm. A concentrate and a diluate cell together form a cell pair. The voltage drop across one cell pair in a typical electrodialysis desalination process is in the range of 0.5 - 1.5 V[2]. The current density depends on the concentration of the feed solution and the diluate. It is in the range of 5 - 50 mA/cm^2. Since in commercial electrodialysis units the area of a cell is in the range of 0.5 - 1.5 m^2 the current through a stack is in the range of 5 - 150 A direct current and the voltage drop over an entire stack is in the range of 100 - 300 V.

2. The basic process parameters

The technical feasibility of electrodialysis as a mass separation process, i. e., its capability of separating certain ions from a given mixture with other molecules, is determined by the ion-exchange membranes used in the system. The economics of the process is mainly determined by the energy consumption and the investment costs for plants, which again are a function of the membrane properties used in the process and various design parameters such as cell dimensions, feed flow velocity, pressure drop of the feed solution in the cell, etc.

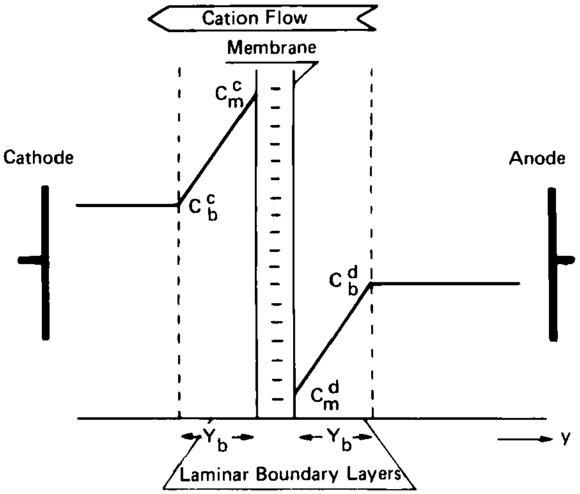


FIGURE 3

Schematic diagram showing concentration polarization effects in the laminar boundary layers of a cation-exchange membrane during electrodialysis. C_b^d and C_b^c are the cation concentrations in the bulk solution of the diluate and concentrate cells, respectively; C_m^d and C_m^c are the cation concentrations in the corresponding cells at the membrane surface.

2.1 Mass transfer through permselective membranes and the limiting current density

Since the permeability of an ion-exchange membrane usually is significantly higher than that of the adjacent solution, the transport of charged particles through a set of ion-exchange membranes leads to a decreased concentration of counter-ions in the laminary boundary layer at the membrane surface facing the diluate cell and an increase at the surface facing the brine cell. The concentration polarisation due to an increase in the brine at the membrane surface might lead to some precipitation of salt at the surface. The decrease of the counter-ions in the diluate directly affects the limiting current density and increases the electric resistance of the solution in the boundary layer3). The flux of a cation from a solution which is depleted of ions and through the membrane and its adjacent laminary boundary layers is shown schematically in Figure 3.

The ionic flux through the membranes and the adjacent boundary layers can be described by the following equation:4)

$$J_i = \left(T_i^M - T_i\right)\frac{i}{zF} = -D_i\frac{dC_i}{dy} \quad (i = +,-)\ . \tag{1}$$

Here T_i^M and T_i are the transport numbers of an ion in the membrane and in the solution, respectively, i is the current density, F the Faraday constant, z the electrochemical valence of the ion, D_i the diffusion coefficient of the ion in the solution and dC_i/dy the ion concentration gradient in the laminar boundary layer.

With most ion-exchange membranes the ion-transport number in the membrane is much larger than that in the solution, i. e., $T_i^M > T_i$. Thus, the resistance to mass transfer is much smaller in the membrane than in the solution. This leads to a depletion of ions on one side of the membrane and to an accumulation of ions on the other, resulting in significant concentration gradients within the boundary layers. Eventually a steady state is attained at which diffusion due to the electrical potential gradient is balanced by diffusion due to the concentration gradient, i. e.:

$$\left(T_i^M - T_i\right)\frac{i}{zF} = -D_i\frac{dC_i}{dy}\ . \tag{2}$$

Rearrangement of equation (1) and (2) and integration yields a simple relation between the boundary layer thickness and the current density:

$$i = \frac{zFD_i\,(C_i^b - C_i^M)}{Y_b\,(T_i^M - T_i)}\ . \tag{3}$$

Increasing the voltage in the stack increases the current density and the flux of ion. This flux, however, has to be counterbalanced by the diffusive flux, which will reach a maximum value when the concentration of the solution at the membrane surface C_i^m approaches zero. The current density which can be reached under a given set of experimental conditions in the steady state is referred to as the limiting current density i_{lim}. It is given by:

$$i_{lim} = \frac{z F D_i C_i^b}{Y_b (T_i^M - T_i)} \quad . \tag{4}$$

Here is C_i^b the concentrations of the counter-ions in the bulk solution in the diluate cell. D_i is a diffusion coefficient of the ions in the solution, F the Faraday constant, z the chemical valence, Y_b the thickness of the laminary boundary layer, T_i^M the transfer number of the counter-ions in the ion-exchange membrane, and T_i the transfer number of the counter-ions in the solution. If the limiting current density is exceeded the process efficiency will be drastically diminished due to the increasing electrical resistance of the solution and the dissociation of water, which leads to pH changes and associated operational problems. The limiting current density determines the membrane area required for a certain desalting capacity and, therefore, to a large extent, the investment costs of an electrodialysis plant.

2.2 Membrane permselectivity

The permselectivity of an ion-exchange membrane is mainly accomplished by the exclusion of the co-ions from the membrane phase. This exclusion can mathematically be described for a binary salt, such as sodium chloride, by the following relation:[5)]

$$C_{Co}^M = \frac{C_s^2}{C_R^M} \left(\frac{Y_s}{Y_s^M}\right)^2 \quad . \tag{5}$$

Here C_{Co}^M is the concentration of the co-ion in the membrane, C_s is the concentration of the salt in the solution adjacent to the membrane surface, C_R^M is the fixed ion-concentration of the membrane, Y_s and Y_s^M are the acitivity coefficients of the salt in the solution and in the membrane, respectively. Equation (5) gives a relation between the co-ion concentration in a cation-exchange membrane, the membrane-fixed ion density and the

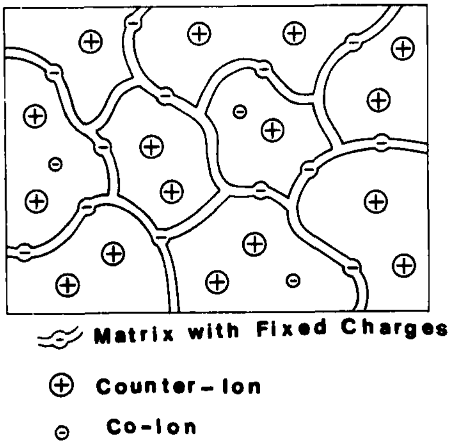


FIGURE 4

Schematic diagram of a cation-exchange membrane.

salt concentration in the adjacent solution. The flux of ions through the membrane is directly proportional to the co-ion concentration in the membrane phase. The ratio of the different ion fluxes then leads to the transport number of different ions in the membrane and with that to the permselectivity of the membrane.3)

2.3 Ion-exchange membranes, their preparation, and properties

The properties and preparation procedures of ion-exchange membranes are closely related to those of ion-exchange resins.5) As in resins, there are two different types of membranes: (1) Cation-exchange membranes which contain negatively charged groups fixed to the polymer matrix and (2) anion-exchange membranes which contain positively charged groups fixed to the polymer matrix. In a cation-exchange membrane the fixed anions are in an electrical equilibrium with the mobile cations in the interstices of the polymer. This is illustrated in Figure 4, which shows schematically the matrix of a cation-exchange membrane with fixed negative charges and mobile cations (the counter-ions). Anions (co-ions) are excluded from the polymer matrix by electrical repulsion.

The most desirable properties of ion-exchange membranes are: (1) High permselectivity, (2) low electrical resistance, (3) good mechanical and form stability, and (4) good chemical stability.
However, these properties are often incompatible, and therefore, difficult to optimize. For instance, increasing the degree of cross-linking improves the mechanical stability but also increases electrical resistance. A high concentration of fixed ionic charges in the membrane matrix leads to a lower electrical resistance but in general causes a high degree of swelling and poor form stability. The properties of ion-exchange membranes are determined by the basic polymer matrix and the type and concentration of fixed ionic moieties. The basic polymer matrix determines the mechanical and chemical properties of the membrane. It often consists of a hydrophobic polymer such as polystyrine, polyethylen, or polysulfone. The type and concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane, but also have a significant effect on the degree of swelling. As fixed charges in cation-exchange membranes the following moieties are generally used: $-SO_3^-$-, $-CO_2^-$-, or $-PO_3^{--}$. In anion-exchange membranes the fixed charges are typically $-NH_3^+$, $>NH_2^+$, and $\geqq N^+$. The sulfonic acid groups are completely dissociated over nearly the entire pH-range, while the carboxilic acid groups are undissociated in the pH-range below 7. The quarternary ammonium groups are completely dissociated over the entire pH-range, but the primary ammonium group is only weakly dissociated. Accordingly, ion-exchange membranes are referred to as having a strong or weak acid or basic character.5)

Most commercial ion-exchange membranes can be distinguished according to the structure and preparation procedure as either homogeneous or heterogeneous membranes. Heterogeneous membranes are usually prepared by embedding ionic particles into an inert binder such as polyethylene, phenolic resins, or polyvinylchloride. The methods of making homogeneous ion-exchange membranes can be summarized in three different categories: 1) Polymerization and polycondensation of monomers, of which at least one must contain a moiety that is, or can be made,

TABLE I

Reported Properties of Commercial Ion-Exchange Membranes

Manufacturer and Designation	Type of Membrane	Area Resistance (Ohm-cm^2)[a]	Transference Number of Counter-ion[b]	Approximate Thickness (mm)
AMF[c]				
C-60	Cat-exch	5	0.80	0.30
A-60	An-exch	6	0.80	0.30
ACI[d]				
CK-1	Cat-exch	1.4	0.85	0.23
DK-1	Cat-exch	1.8	0.85	0.23
CA-1	An-exch	2.1	0.92	0.23
DA-1	An-exch	3.5	0.92	0.23
AGC[e]				
CMV	Cat-exch	3	0.93	0.16
CSV	Cat-exch	10	0.92	0.33
AMV	An-exch	4	0.95	0.16
ASV	An-exch	5	0.95	0.16
IC[f]				
MC-3142	Cat-exch	12	0.94	0.2
MA-3475	An-exch	11	0.99	0.40
DP[g]				
N-901	Cat-exch	3.8	0.96	0.40
II[h]				
CR-61	Cat-exch	11	0.93	0.6
AR-111A	An-exch	11	0.93	0.6
TCS[i]				
CL-2.5T	Cat-exch	3	0.98	0.16
CLS-25T	Cat-exch	3	0.98	0.16
AV-4T	An-exch	4	0.98	0.16
AVS-4T	An-exch	5	0.98	0.16

[a] Measured in 0.5 normal NaCl at 25°C.

[b] Calculated from concentration potentials measured between solutions of 0.5 and 1 normal NaCl.

[c] American Machine and Foundry Co., Stamford, Connecticut.

[d] Asahi Chemical Industry, Ltd., Tokyo, Japan.

[e] Asahi Glass Co., Ltd., Tokyo, Japan.

[f] Ionac Chemical Co., Birmingham, New Jersey, USA.

[g] DuPont Co., Wilmington, DE 19898, USA.

[h] Ionics, Inc., Cambridge, Massachusetts, USA.

[i] Tokuyama Soda Co., Ltd., Tokyo, Japan.

anionic or cationic; 2) Introduction of anionic or cationic moieties into a film by techniques such as inbibing styrine into polymer films. 3) Introducing anionic or cationic moieties into a polymer chain, such as polysulfone followed by the dissolving of the polymer and casting into a film.[5)]

All three preparation methods are used today for making homogeneous ion-exchange membranes for electrodialysis. Usually, the membranes are reinforced by a screen to provide better mechanical stability. Most of todays ion-exchange membranes are prepared as homogeneous structures because of their better overall properties compared to the heterogeneous structures. The properties of some commercial membranes are summarized in Table I. The area resistance measured in a 0.5 normal sodium chloride solution is typically in the range between 1 - 10 Ω cm^2. The transference number measured in two solutions separated by a membrane of 0.5 and 1 n NaCl are typically in the range of 0.8 - 0.95. The thickness of the membrane is typical between 0.2 - 0.5 mm. The list of membranes reported in the table, of course, is far from being complete. There are several more membranes presently on the market or under development.[6)]

2.4 Electrodialysis energy and membrane area requirements

The energy required for the desalination of a solution is given by two terms: (1) The energy required to transfer the ions from the feed solution to the concentrate, and (2) the energy required to pump the solution through the stack. The energy necessary for the ion transfer is directly proportional to the total current flowing through the stack and the voltage drop between the two electrodes and is given by the following equation:

$$E = \frac{I\, n\, R\, t\, z\, F\, Q\, \Delta C}{\xi} \tag{6}$$

Here E is the energy consumption, I the total current flowing through the stack, n is the number of cell pairs in the stack, R the resistance of a cell pair, t the time, F the Faraday constant, z the electrochemical valence, Q the feed solution flow rate, ΔC the concentration difference between the feed solution and the diluate, and ξ the current utilization. The current utilization is directly proportional to the number of cells in the stack and is governed by the current efficiency, which is always less than 1.

Equation (6) indicates that energy required for the transfer of ions from a feed solution into a concentrate is mainly determined by the number of ions transferred (i. e., the concentration difference between the diluate and the feed solution) and the resistance of the stack (i. e., mainly the resistance of the diluate solution). In desalination of brackish water a typical value for the resistance of an electrodialysis cell pair (i. e., the cation- and the anion-exchange membrane plus the diluate and concentrated solution) is 10 - 500 $\Omega \mathrm{cm}^2$.[7)]

The energy necessary for pumping the solutions through the cells is:

$$E_p = k_1 Q_d \Delta P_d + k_2 Q_b \Delta P_b + k_3 Q_c \Delta P_c \qquad (7)$$

Here E_p is the pumping energy, k_1, k_2, and k_3 are constants referring to the efficiency of the pumps, and Q_d, Q_b, and Q_c are volume flow of the diluate, brine, and electrode rinse solutions, respectively. ΔP_d, ΔP_b, and ΔP_e are pressure losses of the flow streams. Energy required for pumping the solutions through the system may become significant or even dominant when solutions with rather low salt concentrations are processed.[2)]

The membrane area required by a certain plant capacity is given by:

$$A = \frac{z F Q \Delta C n}{i \xi} . \qquad (8)$$

Here A is the membrane area, z the electro-chemical valence, F the Faraday constant, Q the volume flow of the product, ΔC the difference in the ion concentration of feed and product, n the number of cells in the stack, i the current density, and ξ the current utilization.

The required membrane area for a certain plant capacity is mainly determined by the current density i and the number of ions removed from the feed solution, which is given by ΔC. The current utilization is given by 3 efficiency terms:

$$\xi = n\,\eta_s \cdot \eta_w \cdot \eta_m \qquad (9)$$

Here ξ is the current utilization, n is the number of cells, η_s, η_w, and η_m are efficiency terms, which are always smaller than 1. η_s refers to the efficiency decrease of the system due to the fact that the membranes are not strictly semipermeable. η_w refers to the efficiency decrease due to the transfer of water through the membrane by osmosis and ion-solvation. η_m refers to the efficiency decrease due to partial electric current flow through the stack manifold. η_w and η_m can be kept close to 1 by an appropriate cell design. η_s is a strong function of the feed solution concentration and can have a significant effect on the efficiency of the process at high feed solution concentrations.

3. Electrodialysis system design and process costs

In addition to the membrane stack, an electrodialysis system consists of several components essential to the proper function of the process. A flow diagram of a typical electrodialysis plant for desalination of brackish water is shown in Figure 5.

The plant consists of a feed water pretreatment system, the membrane stack, and various rinse solution flow circuits. Several variations of this design are possible. One of the more important ones is the so called "reverse polarity" process for which the current polarity is consecutively reversed after certain time intervals ranging from a few minutes to several hours.[8)] Obviously, when the polarity is reversed the hydraulic flow streams are also reversed, i. e., the diluate cells become concentrate cells and vice versa. The advantage of the reverse polarity operating mode is that precipitation in the concentrate cells is minimized.

The total cost of the electrodialysis process is a sum of fixed charges

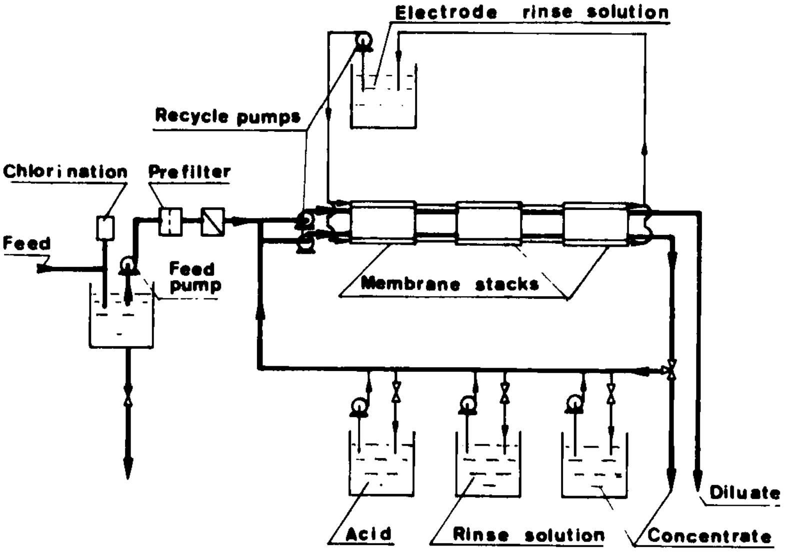


FIGURE 5

Flow diagram of an electrodialysis unit used for brackish water desalination.

associated with amortization of the investment and operating expenses, such as energy, chemical treatment, and labour costs. The investment costs are directly related to the required membrane area, which, as shown above, is a strong function of the feed solution salt concentration. The energy required for the actual desalination process is also directly proportional to the feed solution concentration. Therefore, the total cost of electrodialysis is directly proportional to the feed solution concentration, assuming a fixed product concentration. For desalination of saline water, the cost of electrodialysis is well documented in the literature.9)

A comparison of todays desalination costs of various processes as a function of the feed water salinity is shown in Figure 6. The graphs indicate that for very low salt concentrations in the feed solution ion-exchange is the most economical process, but its costs increase sharply with the feed

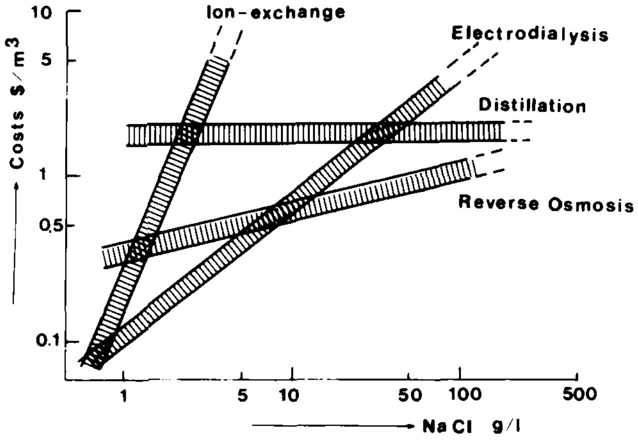


FIGURE 6

Desalination costs for various processes as a function of the feed water salt concentration.

solution salinity and at about 500 ppm salt concentration electrodialysis becomes more economical. With electrodialysis the costs also increasing with feed concentration, and above 5000 ppm reverse osmosis becomes more economical. At very high salt concentrations, in excess of 100 000 ppm, multistage flash evaporation becomes the most economical process. The cost of potable water produced from brackish water sources by electrodialysis is in the range of 0.2 - 0.5 $/m^3 product water.

III. Large Scale Application of Electrodialysis

1. Desalination of brackish water by electrodialysis

The most important large-scale application of electrodialysis is the production of potable water from brackish water sources. Here electrodialysis is competing directly with reverse osmosis and multi-stage flash evaporation. For water with relatively low salt concentration, i. e., less than 5000 ppm, electrodialysis is generally regarded the more economic process, as indicated earlier. One significant feature of electrodialysis is that the salt can be concentrated to comparatively high values without reducing efficiency.[10)] Furthermore, electrodialysis membranes can be operated at elevated temperatures in excess of 40 - 50 °C, which is the temperature of many brackish water sources obtained from deep wells. When the reverse polarity mode is used, precipitation and scaling of divalent ions is less severe in electrodialysis than in reverse osmosis or in evaporation processes.

2. Application of electrodialysis in industrial waste water treatment systems

The treatment of industrial rinse and waste water to recover valuable constituents is a common application of electrodialysis. The reclamation of hydrofluoric acid and sulfuric acid from pickling processes and the removal of heavy metal ions such as cadmium, nickel or copper from electroplating rinse waters are especially attractive. A typical example is indicated in the flow diagram of Figure 7, which shows a cadmium plating line with the plated metal parts transferred from the plating bath to a still rinse and from there to a regular rinse bath. Due to the relatively high salt concentration in the plating bath, there is a considerable carry-over of salts from the plating bath to the still rinse. Therefore, the concentration in the still rinse increases rapidly and frequent treatment of the rinse solution is needed. By installing an electrodialysis unit, as shown in the flow diagram of Figure 7, the salts can be continuously removed from the still rinse and the concentrate recycled directly to the plating bath. The diluate is fed back to the still rinse, thereby keeping its salt concentration at a low level. Substantial savings in rinse water and plating bath consituents can be achieved.

Another application which has been studied on a pilot plant stage is the regeneration of a chemical copper of plating baths. In the production of printed circuits a chemical process is often used for copper plating.[11)] Components which are plated are immersed into a bath containing not only copper ions, but also a complexing agent such as ethylenediamintetraacetic acid (EDTA) and a reducing agent such as formaldehyde. Since the constituents are used in relatively low concentrations the copper content of the bath is rapidly exhausted and copper sulfate must be added

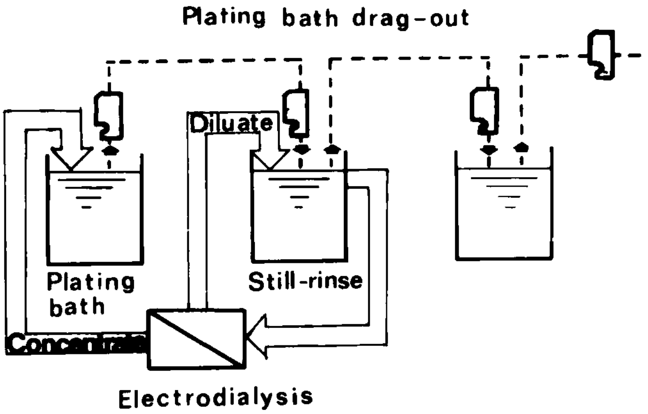


FIGURE 7

Flow diagram showing the installation of an electrodialysis unit for the continuous removal of metal-ions from the still rinse of an electroplating process line.

frequently. During the plating process formaldehyde is oxidized to formiate. After prolonged use the bath becomes enriched with sodium sulfate and formiate and consequently looses its useful properties. By applying electrodialysis in a continuous mode the sodium sulfate and formiate can be selectively removed from the solution without effecting the concentration of formaldehyde and the EDTA-copper complex. Thereby, is the useful life of the plating solution significantly extended. Several other successful applications of electrodialysis in waste water treatment systems which have been studied on a laboratory scale are reported in the literature.11)

3. Electrodialysis in the chemical, food and drug industry

In the food processing industry electrodialysis is used to deionize or deacidify fruit juices, wine, milk, sugar molasses, and whey. Of particular interest is the partial demineralization of whey, which is an excellent source of protein, lactose, vitamins and minerals but is not considered a proper food material because of its high salt content. The partial de-

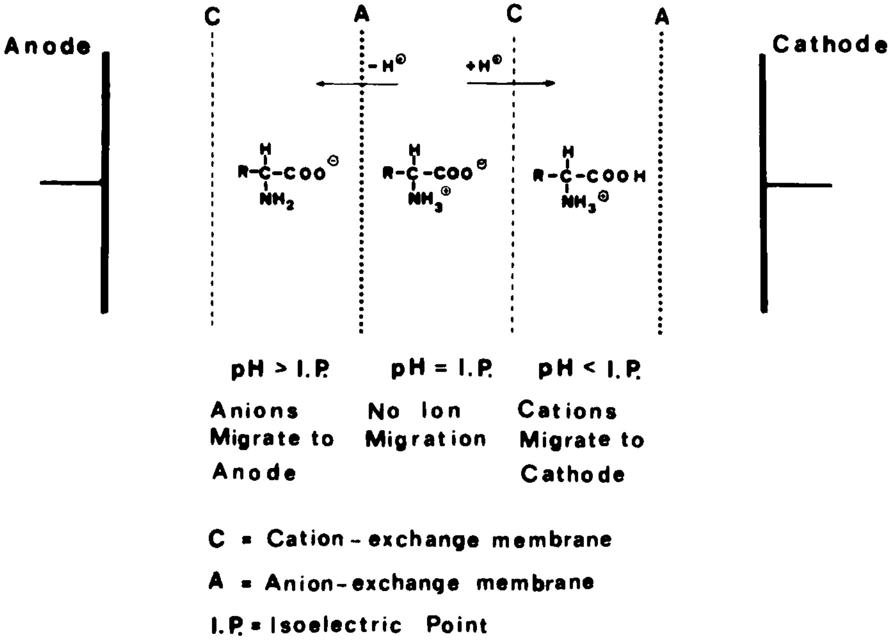


FIGURE 8

Schematic diagram for the migration of an amino acid in a three compartment electrodialysis cell under an electrical potential driving force with the pH-value adjusted in reference to the isoelectric point of the amino acid.

mineralization of whey can be carried out quite efficiently by electrodialysis.[12)] The process has been studied extensively and is now commonly used in the dairy industry. Electrodialysis is also presently used for desalting of molasses in sugar production. In these applications electrodialysis often competes directly with ion-exchange, but in general is less labour-intensive and, because of continuous process design, more reliable and less costly.

In the pharmaceutical industry electrodialysis is used to separate salts, acids, and bases from organic components such as proteins, amino acids, and dextranes. A rather interesting application of electrodialysis is the separation of different amino acids, which because of their amphoteric nature can be protonated when the pH-value of the solution is lower than the isoelectric point thus forming positively charged species. Similarily, for pH-values higher than the isoelectric point negatively charged species are formed. Consequently different amino acids with different isoelectric points can be separated by pH-value adjustment and electrodialysis, as indicated in the flow diagram of Figure 8.

This diagram shows the movement of an amino acid placed in a three-cell compartment between two electrodes. The middle compartment is confined on the anode side by an anion-exchange membrane and on the cathode side by a cation-exchange membrane. If an amino acid is placed in the middle compartment and the pH adjusted, according to its isoelectric point, the amino acid can be either neutral, or positively, or negatively charged, and thus either migrates towards the anode, or towards the cathode, or remains in the middle compartment. This principle can be used for the separation of amino acids which differ significantly in their isoelectric point as indicated in Figure 9.

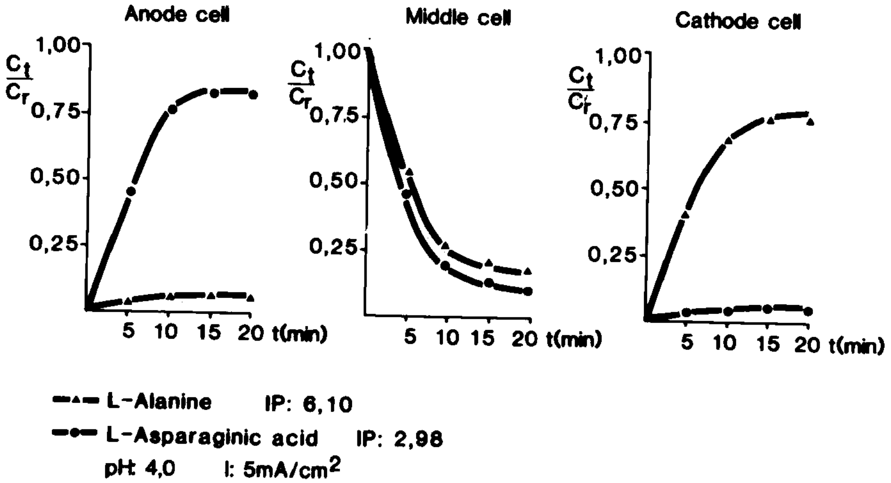


FIGURE 9

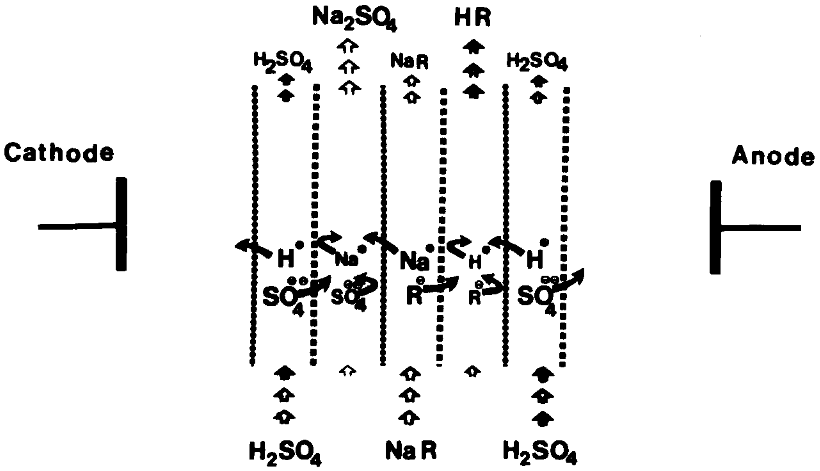
Relative concentrations of L-alanine and L-asparaginic acid in a three cell electrodialysis unit as a function of time.

For example, L-alanine and L-asparagenic acid, which have isoelectric points of 6.1 and 2.98, respectively, can be effectively separated, if a mixture of these two amino acids is placed in the middle cell of the three compartment electrodialysis system shown in Figure 8, and the pH adjusted to 4.0. The L-asparagenic acid will be negatively charged and migrate towards the anode and the L-alanine will be positively charged and migrate towards the cathode. Several other amino acids which have substantial differences in the isoelectric point have been separated by the same procedure.

In the chemical process industry electrodialysis can be used in a slightly modified form to recover organic acids from their salts, as indicated schematically in Figure 10. This figure depicts an electrodialysis unit consisting of a repeating series of four cells. The cells are separated by alternating cation- and anion-exchange membranes. In the first and third cell of a repeating unit streams of sulfuric acid and the salt of the organic acid, respectively, are introduced. By applying an electrical potential difference to the system, the concentrations of H_2SO_4 and NaR in their respective cells are reduced, and sodium sulfate and the organic acid are simultaneously generated in the intervening cells. For this application four independent flow streams are used. An electrodialysis stack providing these features is commercially available today.14)

4. Water dissociation with bipolar membranes

The use of bipolar membranes for the production of protons and hydroxyl-ions is an interesting and economically attractive process which has been explored in recent years on a laboratory scale.15) The principle of water dissociation with bipolar membranes is shown schematically in Figure 11. It is based on the fact that from an aqueous solution placed between a cation- and an anion-exchange membrane all ionic species are removed under the driving force of an electrical potential difference across these two membranes. When all salt ions are removed from this solution the transport of electrical charges through the membranes can only be accomplished by protons and hydroxyl-ions, which are always available in very low concentration. Due to the dissociation equilibrium,



Recovery of organic acids from their salts by electrodialysis

FIGURE 10

Flow diagram for the recovery of an organic acid from its sodium salt by an electrodialytic process utilizing sulfuric acid as a proton source.

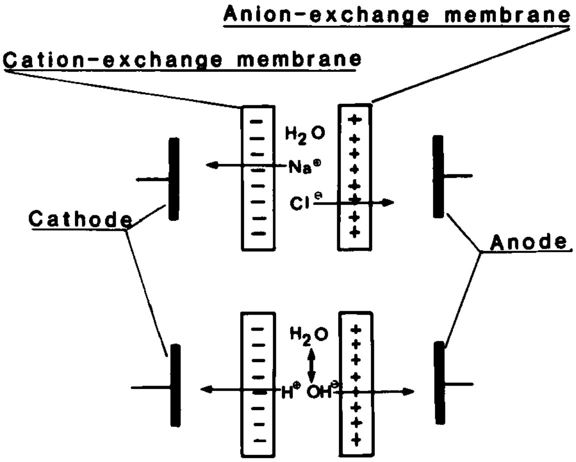
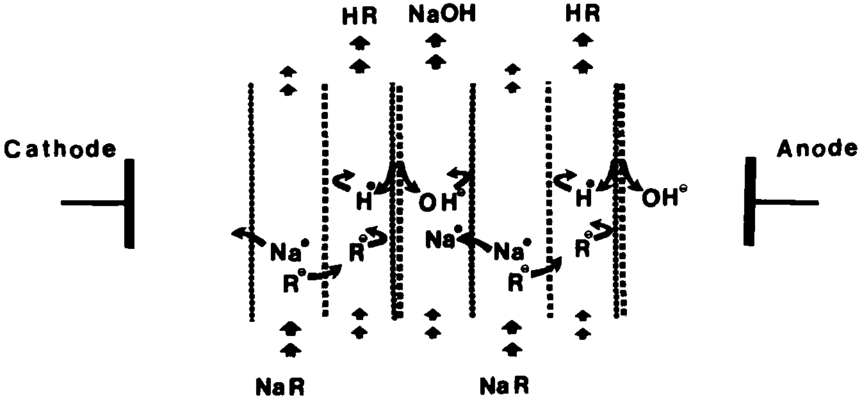


FIGURE 11

Schematic diagram showing the water dissociation in bipolar membranes under the driving force of an electrical potential gradient.

protons and hydroxyl-ions removed from the system will continuously be replenished. Bipolar membranes can be prepared by laminating a cation- and an anion-exchange membrane back to back. The water necessary for dissociation within the bipolar membrane is provided by osmotic effects.

A practical application of the bipolar membrane system is shown in Figure 12. Here an organic acid is recovered from its salt with water being used as the proton source. The figure shows a cell system consisting of an anion-exchange membrane, a bipolar membrane, and a cation-exchange membrane as a repeating unit between the electrodes. The organic salt solution is introduced in the outside cell between the cation- and the anion-exchange membrane. When a direct current is applied, water will dissociate within the bipolar membrane to form an equivalent amount of protons and hydroxyl-ions. The protons will permeate the cation-exchange membrane side of the bipolar membrane and form the organic acid with the anion provided by the organic salt solution in the adjacent cell. The hydroxyl-ions will permeate the anion-exchange side of the bipolar membrane and will form sodium hydroxide, with sodium ions permeating into the cell from the organic salt solution through the adjacent cation-exchange membrane. The net result is the production of sodium hydroxide and the organic acid from the sodium salt of an organic acid. The process can also be used, in principle, for the treatment of concentrated brines obtained from the chemical industry, such as sodium sulfate solutions. In this case electrodialysis with bipolar membranes will produce sulfuric acid and sodium hydroxide. The process has been evaluated extensively on a laboratory scale.16) There are, however, still some significant problems concerning the stability of bipolar membranes. In particular, the anion-exchange side of the membrane, which usually is in contact with a strong alkaline solution, has an unsatisfactory short life expectance. Furthermore, current densities are low and electrical resistances are relatively high. Nevertheless, future improvements in bipolar membranes could result in a very attractive process for the recovery of acids and bases from their salts.



Recovery of organic acids from their salts utilizing bipolar membranes

FIGURE 12

Schematic diagram of an electrodialysis cell arrangement utilizing the water dissociation in bipolar membranes to H^+ and OH^--ions for recovering an organic acid from its sodium salt.

5. Effluent-free regeneration of cation-exchange resins charged with heavy-metal ions

Another interesting application of a modified electrodialysis system is the effluent-free regeneration of cation-exchange resins charged with heavy metal ions. In conventional regeneration of ion-exchange resins an effluent is produced which contains a mixture of the ions used for the regeneration process and the eluated components. With valuable or highly toxic materials, such as certain heavy metal ions, it is desirable to recover these ions in a highly concentrated form with a minimum of impurities. An effluent-free regeneration of charged ion-exchange resins with the extracted metal in solid form can, in some cases, be achieved by a procedure referred to as electrodialytical regeneration. The principle of the process is shown schematically in Figure 13. A cation-exchange resin which is charged with metal ions is placed between two cation-exchange membranes and two electrodes. The electrode compartments contain electrolyte solutions to provide the necessary conductivity. By applying a direct current H-ions generated at the anode will migrate through the first membrane into the resin and replace the metal ion which will then migrate through the second membrane and to the cathode where they are electrochemically reduced and precipitated as solid metal. The process can be continued until most of the metal ions in the resin are replaced by protons and precipitated at the cathode. Ideally the electric current to the cathode is carried by the metal ions, yielding a current utilization for the regeneration process close to 100 %. In practice, however, this is never achieved because of the high mobility of the protons in the resin compared to the metal ions. The process has been studied extensively on a laboratory scale[17)] and shows considerable potential for the recovery of certain heavy metal ions. Of particular interest is the recovery of copper, cadmium, and lead from effluents of the electroplating and lead battery industries.

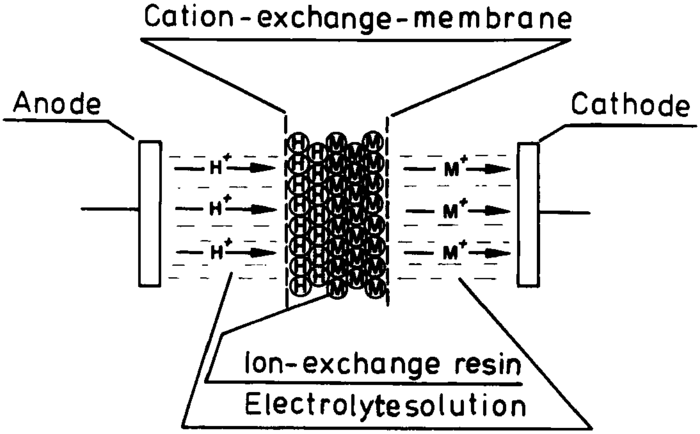


FIGURE 13

Schematic diagram showing the regeneration of an ion-exchange resin charged with heavy metal ions and placed between cation-exchange membranes under the driving force of an electrical potential difference.

There are many more possible applications of electrodialysis in waste water treatment systems, in the chemical and pharmaceutical industry, and in biotechnology which have been evaluated on a laboratory scale. Recent developments in membrane and cell designs$^{18)}$ have provided the basic tools for a significantly wider application of electrodialysis in future years.

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