ELECTRODIALYSIS APPLICATIONS IN THE FOOD INDUSTRY

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ABBREVIATIONS

A_m	Overall membrane surface area ($= N_{cell}\ a_{mg}$)
A_k	Generic k-th empirical constant in Eq. 9
a_{ERS}	Exposed surface area of the electrodes (m^2)
a_i	Activity of species i (dimensionless)
a_k	Effective surface area involved in the ion flow pattern (m^2)

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a_{me}	Effective membrane surface area (m^2)
a_{mg}	Geometrical membrane surface area (m^2)
C	Weight concentration ($\mathrm{kg/m}^3$)
c	Molar concentration ($\mathrm{kmol/m}^3$)
$c^{\pm}$	Anion or cation molar concentration in solution ($\mathrm{kmol/m}^3$)
c_{Cl^-}	Molar concentration of chloride ions in the electrode channels ($\mathrm{kmol/m}^3$)
D_{B}	Solute diffusion coefficient (m^2/s)
D_{B0}	Solute diffusion coefficient at infinite dilution (m^2/s)
d_{e}	Equivalent diameter of ED channel (m)
d_{eR}	Reference equivalent diameter of ED channel (m)
E	Overall potential drop across an ED stack (V)
E_{T}	Thermodynamic electrode potential (V)
E_{T}^{0}	Standard thermodynamic electrode potential at 25°C and unit activity (V)
E_{D}	Donnan potential difference across membranes (V)
E_{d}	Thermodynamic cell potential difference (V)
E_{el}	Electrode potential for anode and cathode processes (V)
E_{j}	Junction potential difference across the boundary layers (V)
E_{MP}	Potential drop across an ED membrane pack (V)
F	Faraday's constant (96,486 C/mol)
h	Channel interval (m)
I	Electric current intensity (A)
$J^{\pm}$	Ion flux in solution ($\mathrm{mol\ m^{-2}s^{-1}}$)
J_{B}	Overall solute permeation flux ($\mathrm{mol\ m^{-2}s^{-1}}$)
J_{W}	Overall water flux ($\mathrm{mol\ m^{-2}s^{-1}}$)
J_{Wd}	Water flux due to osmosis ($\mathrm{mol\ m^{-2}s^{-1}}$)
j	Electric current density ($\mathrm{A/m}^2$)
k_{m}	Solute mass transfer coefficient (m/s)
L	Overall energy consumption in an ED stack (J)
L_{B}	Membrane constant for solute transport by diffusion (m/s)
L_{p}	Membrane hydraulic permeability ($\mathrm{mol\ m^{-2}s^{-1}bar^{-1}}$)
L_{W}	Membrane constant for water transport by diffusion (m/s)
M_{B}	Solute molecular mass (g/mol)
m	Solute molality (mol/kg)
m_e	Theoretical amount of equivalents transported to an electrode (eq)
m_{F0}	Initial solute mass in the feed (kg)
N_{cell}	Overall number of cell pairs (dimensionless)
N	Number of electrons participating in the electrode reaction (dimensionless)
n_{B}	Solute mass (mol)

n_W	Water mass (mol)
Q	Electrical charge passed through a cell (C)
R	Overall electric resistance of the membrane stack (Ω)
Re	Reynolds number (defined in Table III; dimensionless)
R_{ERS}	Electric resistance of electrode rinsing solution (Ω)
R_f	Boundary layer electric resistance (Ω)
R_{fg}	Electric resistance of the fouling gel layer (Ω)
R_G	Gas-law constant ($= 8.314$ J mol^{-1}K^{-1})
R_K	Electric resistance of the bulk solution in the k-th compartment (Ω)
R_k	Electric resistance of the k-th electromembrane (Ω)
R_{MP}	Apparent membrane pack electric resistance (Ω)
r_k	Generic electromembrane surface resistance (Ωm^2)
s	Thickness of a generic electrolytic layer (m)
Sc	Schmidt number [$= \eta/(\rho D_B)$; dimensionless]
Sh	Sherwood number ($= k_m\, h/D_B$; dimensionless)
s_i	Stoichiometric coefficient of species i involved in the electrode reaction (dimensionless)
T_K	Absolute temperature (K)
$t^{\pm}$	Ion transport numbers in solution (dimensionless)
$t_m^{\pm}$	Ion transport number in a generic electromembrane (dimensionless)
t_s	Effective cation- ($t_c^{+} - t_a^{+}$) or anion- ($t_a^{-} - t_c^{-}$) transport number (dimensionless)
t_W	Water transport number (dimensionless)
V_W	Molar volume of pure water (m^3/mol)
v_S	Superficial flow velocity (m/s)
W	ED channel width (m)
x	Generic spatial coordinate (m)
$z^{\pm}$	Ion charge number (dimensionless)

Greek Symbols

α_k	Empirical k-th constant in Eq. 17 (dimensionless)
α_m	Membrane perm-selectivity (dimensionless)
β_k	Generic k-th empirical constant in Eq. 4
$\gamma^{\pm}$	Mean molal activity coefficient (dimensionless)
Δc_B	Difference in solute concentrations in C and D compartments ($= c_{BC} - c_{BD}$) (mol/m^3)
Δl	Separation length between successive eddy promoters (m)
Δm_B	Solute mass transferred into compartment C (kg)
ΔP	Transmembrane pressure difference (MPa)
$\Delta \pi$	Osmotic pressure difference (MPa)

δ	Diffusion boundary layer thickness (m)
δ_{gel}	Gel layer thickness (m)
ε	Specific energy consumption (kWh/kg)
ε_S	Volume fraction of spacer (dimensionless)
ζ	Solute recovery efficiency (dimensionless)
η	Dynamic viscosity (Pa s)
η_r	Relative viscosity ($= \eta/\eta_W$; dimensionless)
Ψ_{ED}	Electrodialysis membrane-fouling index (Ω/A)
θ	Time (s)
θ'	Dummy variable of integration (s)
Λ	Equivalent conductance (S m^2/keq)
Λ_0	Equivalent conductance at infinite dilution (S m^2/keq)
$\lambda^{\pm}$	Equivalent ion conductance (S m^2/keq)
$\lambda_0^{\pm}$	Equivalent ion conductance at infinite dilution (S m^2/keq)
ρ	Density (kg/m^3)
σ	Reflection coefficient (dimensionless)
χ	Electric conductivity (S/m)
Ω	Total current efficiency (dimensionless)
Ω_C	Faraday efficiency (dimensionless)
Ω_L	Current leakage efficiency (dimensionless)

Subscripts

a	Referred to the anion-exchange membrane
B	Referred to solute
c	Referred to the cation-exchange membrane
C	Referred to the concentrating compartment
D	Referred to the diluting compartment
e	Effective
ERS	Referred to electrode-rinsing solution
g	Geometric
gel	Referred to the gel layer
lim	Limiting
m	Referred to the membrane surface
max	Referred to the theoretical maximum concentration
W	Referred to water

This paper reviews the most recent innovations in electrodialysis (ED) modules and/or processes that appear to affect the food and drinks industries in the short-medium term, together with their basic mass transport equations that might help ED unit design or optimization. Future perspectives for ED processing in the food sector are also outlined.

I. INTRODUCTION

Electrodialysis (ED) is a unit operation for the separation or concentration of ions in solutions based on their selective electromigration through semipermeable membranes under the influence of a potential gradient (Lacey and Loeb, 1972; Strathmann, 1992). Owing to their selectivity, ion-exchange membranes (IEM) allow transport of only cations (cation-exchange membranes) or anions (anion-exchange membranes) and thus can be used to concentrate, remove, or separate electrolytes.

Despite the first industrial ED application in the food sector dated back to 1960 and concerned the demineralization of cheese whey for use in baby foods, the history of ED is longer than that usually acknowledged (Shaposhnik and Kesore, 1997).

A technique combining dialysis and electrolysis was first proposed to de-ash sugar syrup by Maigrot and Sabates (1890). The archetype consisted of two carbon electrodes piloted by a dynamo and separated by a permanganate paper-based membrane. Once the sugar syrup had been poured into the central anodic compartment and the dynamo had been turned on, potassium, sodium, magnesium, and calcium cations tended to migrate into the cathodic compartment. By controlling the pH in this compartment via the so-called litmus paper, it was possible to prevent sparingly soluble hydroxides from precipitating. Thus, as the indicator turned blue, the ED process was stopped.

In 1939, Manegold and Kalauch assembled a three-compartment ED apparatus consisting of a permselective anion-exchange membrane and a cation-exchange one. It was, however, only in the early 1950s that the manufacture of selective membranes from ion exchangers allowed the multicompartment electrodialysers to be assembled (Shaposhnik and Kesore, 1997).

The development of such membranes in England and the United States was not an easy task, as finely outlined by Solt (1995). In those days, the combined efforts of the Netherlands National Research Organisation (TNO) and the South African Council for Scientific and Industrial Research resulted in the development of the ED process for demineralizing saline waters from mines. In the late 1950s, the Office of European Economic Cooperation, as well as in the 1960s the Institute for Arid Zone Research at Beersheva (Israel) and several Japanese manufacturers, contributed to further R&D in this sector (Lacey and Loeb, 1972; Solt, 1995).

The first scientific paper on ED was published in 1903 by Morse and Pierce (Shaposhnik and Kesore, 1997), but the quantitative theory of charged membranes was available only 50 years later (Teorell, 1953). It incorporated the electrostatic repulsion of co-ions from the fixed charges of the membrane, as predicted by the thermodynamical theory of membrane equilibrium developed by Donnan (1911).

The present largest area of application for ED is in the desalination of brackish water for the production of potable water (Audinos, 1992; Strathmann, 1992) and de-ashing of milk whey to obtain valuable raw materials for baby foods (Batchelder, 1987). However, ED applications are still in their infancy and ED-processing potentialities have not been completely exploited probably because of the high specific electromembrane costs or their short lifetime (this being not longer than 1 year, especially if the feed solution is fouling or ED separation plant has not been well designed or is not properly conducted).

The main aim of this paper was to review the present and potential ED applications that appear to be of particular interest for the food and drinks sector in the short-medium term, as well as the basic mass transport equations that might help ED unit design or optimization.

II. ED PRINCIPLES

A. BASIC CONCEPTS AND DEFINITIONS

For a better comprehension of the ED processes it is necessary to refresh a few basic concepts and definitions regarding the electrolytic cell and thermodynamic electrode potential, Faraday's laws, current efficiency, ion conduction, diffusivity, and transport numbers in solution.

An electrolytic cell is essentially composed of a pair of electrodes submerged into an electrolyte for conduction of ions and connected to a direct current (DC) generator via an external conductor to provide for continuity of the circuit. The electrode connected to the positive pole of the DC generator is called anode, while that linked to the negative one, cathode. The current flow in an electrolyte results from the movement of positive and negative ions and is assumed as positive when directed as the positive charges or opposite to the electrons in the external circuit. When the cell is not operating under conditions of standard concentration, the thermodynamic electrode (or cell) potential (E_{T}) can be estimated from the Nernst equation:

$$E_{\mathrm{T}} = E_{\mathrm{T}}^{0} - \frac{R_{\mathrm{G}} T_{\mathrm{K}}}{nF} \ln\left(\prod_{i} a_i^{s_i}\right) \tag{1}$$

where E_{T}^{0} is the standard potential at 25°C and unit activity, a_i is the activity of species i, s_i the corresponding stoichiometric coefficient, which is positive for products or negative for reactants, F the Faraday's constant (= 96,486 C mol^{-1}), R_G the universal gas constant (= 8.31 J $\text{mol}^{-1}\text{K}^{-1}$), T_K the absolute temperature, and n the overall number of electrons participating in the reaction (Prentice, 1991).

Thus, in a cell supplied with two graphite electrodes submerged into a brine solution, the following electrode reactions may be accomplished:

$$\text{Cathode: } 2H_3O^+ + 2e^- = H_2\uparrow + 2H_2O$$

$$\text{Anode: } 2Cl^- = Cl_2\uparrow + 2e^-$$

The evolution of H_2 and Cl_2 transforms the cathode into a hydrogen electrode and the anode into a chlorine one (Prentice, 1991), thus resulting in an electrochemical cell with a thermodynamic cell potential difference (E_d) at 25°C equal to:

$$E_d = 1.358 + 0.059 \quad \text{pH} - 0.059 \ \log c_{Cl^-} \tag{2}$$

where c_{Cl^-} is the molar concentration of chloride ions in the electrode channels. So, when using an electrode-rinsing solution at 0.5 kmol/m^3 and an initial pH value of about 6.5, the cell potential difference is initially equal to 1.76 V. As the H_3O^+ reduces at the cathode, its concentration reduces, thus increasing the pH value and cell potential difference (E_d).

According to Michael Faraday, the theoretical amount of equivalents (m_e) of the product transported to one or another electrode is directly proportional to the electric charge (Q) passed through the cell:

$$m_e = \frac{Q}{F} = \frac{\int_0^{\theta} I \, d\theta'}{F} \tag{3}$$

where θ is the time elapsed. In real electrolytic processes some of the charge is consumed in parasitic processes or other deviations are to be accounted for. Thus, the ratio between the effective and theoretical amounts of equivalents transported is a measure of the process efficiency, that is the so-called current or Faraday efficiency (Ω).

The specific conductivity (χ) is a measure of the mobility of ions in an electrolyte or electrons in a metallic conductor. Thus, χ is about 1 or 10^7 S/m for a 0.1 kmol/m^3 aqueous salt solution or for a metal such as iron, respectively. Such a difference in charge mobility makes the temperature dependence of χ [i.e.,$(1/\chi)\partial\chi/\partial T_K$] positive for ions of about 2.5% per K, but negative for metals and alloys of approximately an order of magnitude lower (Prentice, 1991).

In aqueous systems χ is proportional to the bulk electrolyte concentration (c_B) in dilute solutions, reaches a maximum, and then decreases due to ion association and viscosity effects. Friedrich Kohlrausch found useful to introduce a conductivity function not changing abruptly with c_B, that is, the so-called *equivalent conductance* (Λ), defined as the ratio between χ and c_B, the latter being expressed in equivalents per unit volume. Because of incomplete dissociation at higher concentrations and higher electrolyte viscosity, Λ decreases at higher c_B values. Empirically, it was observed a linear relationship between Λ and the square root of c_B, which is generally known as the Kohlrausch limiting law. As an example, Figure 1 shows its validity either for a strong electrolyte (i.e., NaCl) or for the sodium salts of a few weak monocarboxylic acids such as acetic and propionic acids. For $c_B > 0.1$ mol/m^3 Kohlrausch limiting law is generally regarded as inadequate to describe the variation of Λ with c_B (Robinson and Stokes, 2002) and it may be empirically expanded in powers of $\sqrt{c_B}$ as follows:

$$\Lambda = \frac{\chi}{c_B} = \Lambda_0 + \beta_1 c_B^{1/2} + \beta_2 c_B + \beta_3 c_B^{3/2} \tag{4}$$

where β_i is a generic coefficient and Λ_0 is the equivalent conductivity at infinite dilution.

Since the current results from the motion in opposite directions of anions and cations, Λ can be considered as the sum of two ionic conductivities:

$$\Lambda = \lambda^+ + \lambda^- \tag{5}$$

According to Kohlrausch's law of the Independent Migration of Ions the equivalent conductivity at infinite dilution of a cation (${\lambda_0}^+$) or an anion (${\lambda_0}^-$) depends only on the nature of the ion and properties of the medium, such as

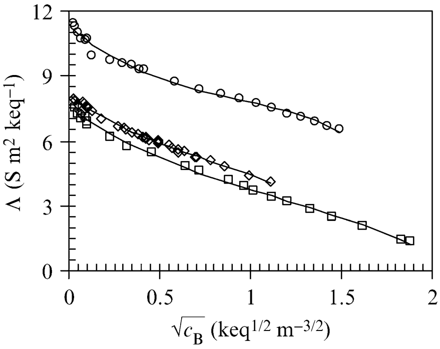

FIG. 1 Equivalent conductance (Λ) for sodium chloride (○), sodium acetate (◇), and sodium propionate (□) at 20°C against the square root of solute concentration ($\sqrt{c_B}$), as extracted from Fidaleo and Moresi (2005a,b, 2006). The continuous lines were calculated using Eq. 4 and the empirical parameters Λ_0 and β_i extracted from Fidaleo and Moresi (2005a,b, 2006).

TABLE I

EQUIVALENT CONDUCTIVITY AT INFINITE DILUTION OF SELECTED CATIONS ($\lambda_0{}^+$) AND ANIONS (λ_0^-) IN WATER AT 25 °C[a]

Anion	λ_0^- (S m^2 keq^{-1})	Cation	λ_0^+ (S m^2 keq^{-1})
OH^-	19.76	H^+	34.98
Cl^-	7.63	Na^+	5.01
NO_3^-	7.14	K^+	7.35
SO_4^{2-}	8.00	NH_4^+	7.34
HCO_3^-	4.45	Mg^{2+}	5.31
CH_3COO^-	4.09	Ca^{2+}	5.95

[a] As extracted from Prentice (1991) and Reid *et al.* (1987).

temperature and viscosity, since each ion is moving in a medium where the ions are so far apart they do not interfere one another. Table I shows the equivalent conductivity at infinite dilution of a few ions at 25 °C, as extracted from Prentice (1991) and Reid *et al.* (1987). Generally speaking, such a parameter is of the order of 5 S m^2/keq with notable exceptions for hydrogen and hydroxyl ions (Table I).

The transport (or transference) numbers ($t^{\pm}$) represent the fractions of current carried out by such specific ions in the absence of concentration gradients. In dilute solutions $t^{\pm}$ can be estimated by dividing the equivalent ion conductance ($\lambda_0^{\pm}$) by Λ_0. When concentration gradients are present, some of the current arises from diffusion and this affects the effective $t^{\pm}$ numbers. Generally, the transference numbers are weak functions of concentration and temperature and may be regarded as practically independent of salt concentration (Prentice, 1991; Robinson and Stokes, 2002).

As an example, by referring to Figure 1, it is possible to determine the limiting conductivity for NaCl by extrapolating the Λ versus $\sqrt{c_B}$ plot for c_B tending to zero ($\Lambda_0 = 11.33 \pm 0.09$ S m^2/keq) and to extract the limiting conductance for Na^+ from literature ($\lambda_0{}^+ = 4.495$ S m^2/keq at 20 °C). Thus, the transport number for sodium ion (t^+) can be directly estimated as 0.397, while that for the chloride ion (t^-) is 0.603 since the sum of the transport numbers must equal one (Prentice, 1991; Robinson and Stokes, 2002). This means that Na^+ ions carry about 40% of the current, whereas the Cl^- ions the remaining 60%. Thus, the ion flux in solution resulting from the applied electric field, in the absence of concentration gradients, can be predicted as:

$$J^{\pm} = \frac{t^{\pm}}{F} j \qquad (6)$$

where j is the electric current density.

The mechanism of ion transport is altered by the contribution of diffusion. To account for this effect, it is necessary to know the electrolyte diffusivity. The diffusion coefficient (D_{B0}) at infinite dilution can be estimated via the Nernst-Haskell equation (Reid *et al.*, 1987):

$$D_{B0} = \frac{R_G T_K}{F^2} \frac{2}{\frac{1}{\lambda_0^+} + \frac{1}{\lambda_0^-}} \tag{7}$$

In the concentration range regarding the ED processes, the effective diffusion coefficient (D_B) can be predicted via the Gordon relationship (Reid *et al.*, 1987), which accounts for the partial derivative of the natural logarithm of the mean molal activity coefficient ($\gamma^{\pm}$) with respect to molality (m) and solvent relative viscosity (η_r):

$$D_B = \frac{D_{B0}}{\eta_r}\left(1 + m\frac{\mathrm{dln}\,\gamma^{\pm}}{\mathrm{d}m}\right) \tag{8}$$

Figure 2 shows $\gamma^{\pm}$ for a few electrolytes as a function of m, as extracted from Robinson and Stokes (2002), as well as their calculated values using the Debye-Hückel model integrated with a linear function of m to extend its accuracy beyond the dilute region:

$$\ln \gamma^{\pm} = \frac{-A_1\sqrt{m}}{1 + A_2\sqrt{m}} + A_3 m \tag{9}$$

In this way, it was possible to correlate $\gamma^{\pm}$ data for the above-mentioned electrolyte solutions with molality up to 2.5–6 mol/kg (Figure 2). For the

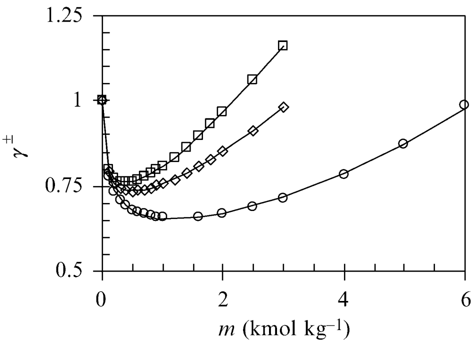

FIG. 2 Effect of solute molality (m) on the mean molal activity coefficient ($\gamma^{\pm}$) for sodium chloride (○), sodium acetate (◇), and sodium propionate (□) at 25°C, as extracted from Robinson and Stokes (2002). The continuous lines were calculated using Eq. 9 and the empirical coefficients A_i extracted from Fidaleo and Moresi (2005a,b, 2006).

NaCl solutions, when setting A_1, A_2, and A_3 equal to 0.979 $kg^{1/2}/mol^{1/2}$, 0.732 $kg^{1/2}/mol^{1/2}$, and 0.139 kg/mol, respectively (Fidaleo and Moresi, 2005a), the average experimental error was as little as 0.6%, about an order of magnitude lower than the average error (5%) pertaining to the well-known correlation by Bromley (1973).

B. ELECTROMEMBRANES

1. *Monopolar membranes*

The IEM used in ED are essentially sheets of ion-exchange resins (IER). Whereas IERs are generally weak and dimensionally unstable for they may adsorb different amounts of water depending on pH, electrolyte concentration, and temperature, the IEMs possess greater mechanical strength and flexibility as conferred by appropriate reinforcing materials. The commercially available IEMs can be subdivided into two major categories, either homogeneous or heterogeneous (Strathmann, 1992).

Homogeneous IEM are produced either by polymerization of functional monomers (e.g., polycondensation of phenol or phenol-sulphonic acid with formaldehyde) or by functionalization of a polymer film by sulphonation of a polystyrene film.

Heterogeneous IEMs are produced by melting and pressing of dry IERs with a granulated polymer or by dispersion of IERs in a solution or a melted polymer matrix. To present a low electrical resistance, such membranes have to contain more than 65% w/w of cross-linked ion-exchange particles, resulting in inadequate mechanical strength and dimensional instability. Thus, the heterogeneous membranes usually hold a higher electrical resistance and a more uneven distribution of fixed charges than the homogeneous ones.

Owing to the negatively (e.g., $–SO_3^-$, $–COO^-$, $–PO_3^{2-}$, $–HPO_2^-$) or positively (e.g., $–NH_3^+$, $–RNH_2^+$, $–R_3N^+$, $–R_2N^+$, where the R group generally coincides with the methyl one, $–CH_3$) charged groups chemically attached to the resin matrix, an IEM can be classified as a *cationic* membrane or an *anionic* one, respectively. It allows intrusion and exchange of counterions from an external source, as well as exclusion of the co-ions, that is the ions with a charge opposite or equal to its fixed charge, respectively (Figure 3). Such membranes are monopolar since they are permeable to a single type of ions only.

Whatever the IEM, counterions carry most of the electric current, the concentration of co-ions being relatively low within the membrane itself. Moreover, the fixed ions are in electroneutrality with mobile ions in the interstices of the membrane and repel the co-ions, this type of action being usually called Donnan exclusion.

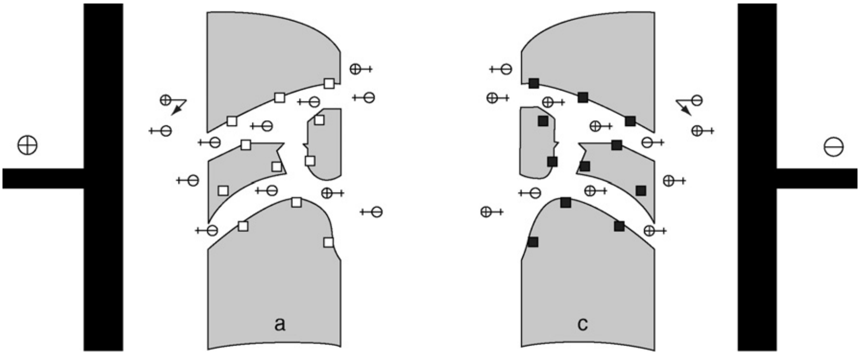

FIG. 3 Schematic diagram of the internal structure of anionic (a) and cationic (c) membranes and their operation under the influence of an electric field: ○, mobile anions (−) and cations (+); □, positive fixed charge; ■, negative fixed charge.

Ion-exchange polymers, such as polystyrene sulphonic acid, are water soluble, so cross-linking with divinylbenzene (DVB) is used to prevent dissolution of ion-permeable membranes. As the degree of cross-linking is increased, the membrane selectivity, stability, and electrical resistance increase. On the contrary, as the fixed-charge density is increased, there is a positive effect on membrane selectivity and conductivity, but a negative one on membrane swelling. Thus, a compromise among selectivity, electrical resistance, and dimensional stability has to be achieved by controlling appropriately cross-linking and fixed-charge densities.

Also the different ionic groups significantly affect the selectivity and electric resistance of IEMs. For instance, the sulphonic acid ($\text{–}SO_3^-$) or quaternary ammonium ($\text{–}R_3N^+$) group is completely dissociated over the entire pH range, while the primary ammonium group ($\text{–}NH_3^+$) is only weakly dissociated and the carboxylic one ($\text{–}COO^-$) is virtually undissociated for $pH < 3$ (Strathmann, 1992).

IEMs can be discriminated according to their mechanical and electrical properties, perm-selectivity, and chemical stability.

First, to distinguish an anion-exchange membrane from a cation-exchange one, it is sufficient to drip a few drops of 0.05% solution of methylene blue and methyl orange on the top of any of them and to note whether the color of the resulting stain tends to a golden yellow or a deep blue, respectively (Strathmann, 1992).

Second, an efficient use of such membranes asks for the absence of pinholes, this being easy to check via the following procedure (Strathmann, 1992):

A. Place a wet membrane sheet on a white absorbent paper sheet.
B. Spread a few drops of 0.2% (w/v) solution of methylene blue or erythrocin-B over the entire surface of the anionic or cationic membrane, respectively.
C. Remove the membrane and check whether the paper sheet has been stained.

Lack of dyed spots on the white paper assures the membrane is free of pinholes.

The membrane swelling capacity (or gel water content) is defined as the percentage ratio of the difference between the mass of a wet sample (m_W), equilibrated in deionized water for 2 days, and that of the same sample (m_D), dried at 75°C over phosphorous oxide (P_2O_5) under vacuum, by m_D (Strathmann, 1992).

The ion-exchange capacity (IEC) of a charged membrane can be determined as follows:

A. Equilibrate a sample of anionic or cationic membrane in 1 kmol/m^3 HCl or NaOH, respectively, for about 24 hours.
B. Rinse the sample with deionized water for about 24 hour.
C. Titrate the sample with 1 kmol/m^3 NaOH or HCl, respectively.
D. Dry the sample at 75°C over P_2O_5 under vacuum and weight it (m_D).
E. Refer the equivalents of alkali or acid used to m_D.

The membrane perm-selectivity (α_m) is defined as the ratio between the actual and theoretical transfer of counterions through any IEM. It can be simply determined as the percentage ratio between the experimental and theoretical Donnan potential differences as measured using a test system consisting of two cells provided with calomel electrodes and filled with well-mixed standardized aqueous solutions of KCl (at 0.1 and 0.5 kmol/m^3), kept at 25°C, and separated by the IEM sample under testing.

The area resistance (r_m) of a charged membrane is indirectly measured using a conductivity cell composed of two well-stirred chambers containing two electrodes submerged into an aqueous solution of NaCl (0.5 kmol/m^3). The electric conductivity of the cell is determined in presence or absence of a generic IEM sample in a bridge circuit using alternating current and both measures allow the membrane area resistance to be calculated using the second Ohm's law (Strathmann, 1992). This value is generally provided by the manufacturer (Table II) and is to be multiplied by 1.75 to estimate roughly the membrane surface resistance to DC (Davies and Brockman, 1972).

The long-term chemical stability of the electromembranes affects the economics of any ED application and is generally determined by assessing

TABLE II

MAIN CHARACTERISTICS[a] OF SOME REPRESENTATIVE COMMERCIALLY AVAILABLE ION-EXCHANGE MEMBRANES[b]

Membrane	Type	Main properties	Category	Thickness (mm)	Burst strength (bar)	IEC (meq/g)	Gel water (%)	r_m (Ω cm^2)	α_m (%)
ASAHI GLASS ENGINEERING Co. (Chiba-shi, Chiba, Japan)									
SELEMION (http://www.agc.co.jp/english/chemicals/ion-maku/selemion/sele.htm#anchor795659)									
CMV	Cation	Styrene	Homo	0.13–0.15	3–5	2.4	25	2.0–3.5	91
AMV	Anion	Butadiene	Homo	0.11–0.15	2–5	1.9	19	1.5–3.0	93
CMD	Cation		Homo	0.38–0.42	10–20	–	–	8–10	–
AMD	Anion		Homo	0.38–0.42	10–20	–	–	8–10	95
ASTOM Co. (Minato-Ku, Tokyo, Japan; http://www.astom-corp.jp)									
AMF-IPEX (Asahi Chemical Industry Co. Ltd., Chiyoda-ku, Tokyo, Japan; http://www.asahi-kasei.co.jp)									
C-60	Cation	Polyethylene-styrene	Hetero	0.3	3	1.6	35	5	92
A-60	Anion	Polyethylene-styrene	Hetero	0.3	3	2	22	7	93
ACIPEX (Asahi Chemical Industry Co. Ltd., Tokyo, Japan)									
K-101	Cation	Styrene/DVB		0.24	–	1.2	24	2.1	91
A-101	Anion	Styrene/DVB		0.21	–	1.4	31	2–3	45
NEOSEPTA® (Tokuyama Soda Co. Ltd., Nishi-Shimbashi, Minato-ku, Tokyo, Japan; htpp://www.tokuyama.co.jp)									
CMX	Cation			0.17–0.19	5–6	1.5–1.8	25–30	2.5–3.5	98
AMX	Anion			0.16–0.18	4.5–5.5	1.4–1.7	25–30	2.5–3.5	98
CMS	Cation	Univalent		0.14–0.17	3–4	2.0–2.5	35–45	1.5–2.5	98
ACS	Anion	Univalent		0.15–0.20	3–5	1.4–2.0	20–30	2.0–2.5	98
AFN	Anion	Antifouling		0.15–0.20	2–3.5	2.5–3.7	40–55	0.4–1.5	98
AXE 01	Anion	Antifouling 60°C		0.17	4.1	2	–	1.4	–
ELECTROPURE EXCELLION™ (Laguna Hills, CA, USA; http://www.electropure-inc.com/downloads/Excellion%20Specifications.pdf)									
I-100	Cation	100°C	Hetero	0.32–0.34	3.0–3.2	–	–	7.5–12.5	–
A-20	Anion	100°C	Hetero	0.32–0.34	2.8–3.0	–	–	5–10	–
DU PONT Co. (Fayetteville, NC, US; http://www.dupont.com/fuelcells/pdf/nae101.pdf)									
NAFION®									
N 117	Cation	Perfluorinated		0.2	–	0.9	16	1.5	–
N 901	Cation	Perfluorinated		0.4	–	1.1	5	3.8	96

IONICS Inc. (Watertown, MA, US; htpp://www.ionics.com)									
CR61 CZL183	Cation	Polystyrene	Homo	0.6	–	2.7	40	–	–
AR103 PZL183	Anion	Polystyrene	Homo	0.6	–	1.8	43	–	–
61CZL386	Cation			0.6	–	2.7	40	9	–
103QZL386	Anion			0.63	–	2.1	36	6	–
LINAN EURO-CHINA Co. (Linan City, China; http://www.Linanwindow.Com/Qianqiu/Membeng.Htm)									
–	Cation		Hetero	0.42	3.5	2	40–55	15	90
–	Anion		Hetero	0.42	3.5	1.8	30–45	15	88
MEMBRANES INTERNATIONAL Inc. (Glen Rock, NJ, USA; http://www.membranesinternational.com/tech.htm)									
CMI-7000S	Cation	90°C	Hetero	0.45	13.6	1.3	–	40	94
AMI-7001S	Anion	90°C	Hetero	0.45	13.6	1.0	–	85	90
PALL RAI Inc. (Hauppauge, NY, US; http://phychem.kjist.ac.kr/312.pdf)									
R-1010	Cation	Perfluorinated		0.05	–	1.2	20	0.4	94
R-1035	Anion	Perfluorinated		0.05	–	1.0	10	1.3	77
PCA GmbH (Heusweiler, D; www.pca-gmbh.com)									
PC-100D	Anion	Polyester reinforced		0.08–0.10	4–5	1.2	50	5	>93
PC-200D	Anion	Polyester reinforced		0.08–0.10	4–5	1.3	45	2	>93
PCA GmbH (Heusweiler, D; http://www.pca-gmbh.com)									
PC-100D	Anion	Polyester reinforced		0.08–0.10	4–5	1.2	50	5	>93
PC-200D	Anion	Polyester reinforced		0.08–0.10	4–5	1.3	45	2	>93
PERMUTIT Co. (USFilter Corp., Warrendale, PA, US; http://www.usfilter.com/water/Business+Centers/Industrial_Process_Water/Industrial_Process_Water_Products/pw_permutit.htm)									
PERMAPLEX									
C-20	Cation			0.8	–	3	30–40	–	98
A-20	Anion			0.8	–	2	30–40	–	98
RHONE-POULENC CHEMIE GmbH (Frankfurt, D; http://phychem.kjist.ac.kr/312.pdf)									
CRP	Cation			0.6	–	2.6	40	6.3	65
ARP	Anion			0.5	–	1.8	34	6.9	79
SYBRON CHEMICALS Inc. (Birmingham, NJ, US; htpp://www.ion-exchange.com/products/membranes/index.html)									
IONAC									
MC-3470	Cation	80°C	Hetero	0.38	10	1.5	35	10–25	96
MA-3475	Anion	80°C	Hetero	0.41	10	0.9	31	25–50	99

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[a] Type; main properties; category; thickness, burst strength; ion-exchange capacity, IEC; gel water content; area resistance, r_m, at 25°C, 0.5 kmol NaCl/m^3; membrane perm-selectivity, α_m, at 1.0/0.5 kmol/m^3 KCl.

[b] As claimed by the manufacturers or extracted from Elmidaoui *et al*. (2002); Lacey (1972); Lee *et al*. (2002d); Strathmann (1992); and several online publications (http://phychem.kjist.ac.kr/312.pdf; http://phychem.kjist.ac.kr; http://www.pca-gmbh.com).

changes in the membrane mechanical or electrical properties after exposure to acidic or alkaline solutions, as well as oxidizing agents, for prefixed time intervals. For instance, by reducing the DVB content in the resin matrix, it was possible to improve the membrane chemical resistance, thus resulting in an extended membrane life. In the circumstances, the novel IEM labelled as AXE 01 (Eurodia Industrie, Wissous, F) can resist to irreversible organic fouling, since its soaking in aqueous solutions containing 1% (w/w) NaOH and 1% (w/w) NaCl at 60°C for 5 days makes the membrane swell so as to remove easily the organic molecules trapped inside the membrane itself with just a 10% or 20% reduction in IEC or burst strength (Elmidaoui *et al.*, 2002). Moreover, whereas almost all electromembranes operate at temperatures smaller than 40°C, this novel membrane can be operated up to 60°C, thus favoring mass transport while limiting microbial growth in the solutions undergoing ED treatment.

Membrane fouling due to adsorption of polyelectrolytes (such as humic acids, surfactants, and proteins) may severely reduce ion permeability, especially in the anion-exchange membranes. However, exhausted anion-exchange membranes used in the ED of molasses, whey, citric acid, or sodium dodecylbenzenesulfonate can be reactivated by circulating simultaneously an acidic solution in one compartment and an alkaline solution in the other one, both solutions at titres greater than 0.1 kmol/m^3 (Tokuyama Soda Co., 1983).

Table II shows the main characteristics of some representative commercially available IEMs as claimed by the manufacturers or extracted from Elmidaoui *et al.* (2002), Lacey (1972), Lee *et al.* (2002d), Strathmann (1992), and several online publications (http://phychem.kjist.ac.kr/312.pdf; http://phychem.kjist.ac.kr; http://www.pca-gmbh.com).

Finally, the commercial ED membranes made "tight" or "loose" have an average pore size of 1 or 10 nm, respectively. This gives rise to a smaller or a greater permeability toward co-ions. A typical ED membrane has usually a pore size of 1–2 nm with an IEC of 1.6–3.0 meq/g of dry mass of membrane.

a. ED stack construction. An ED system consists of the following items: one or more ED stacks, a DC generator, pumps, piping, tanks, and measuring devices for pressure, temperature, pH, electric conductivity, and flow rate.

The ED stack is the unit holding together anionic and cationic membranes assembled in parallel as in a filter press between two electrode-end blocks in such a manner that the stream undergoing ion depletion (i.e., the *diluate* or *diluting stream*) is kept separated from the other solution (*concentrate* or *concentrating stream*) undergoing ion enrichment. Figure 4 shows an exploded view of it.

The two electrode-end blocks contain the in- and outlet adapters and the electrical connections. They are pressed together by a steel frame to hold the

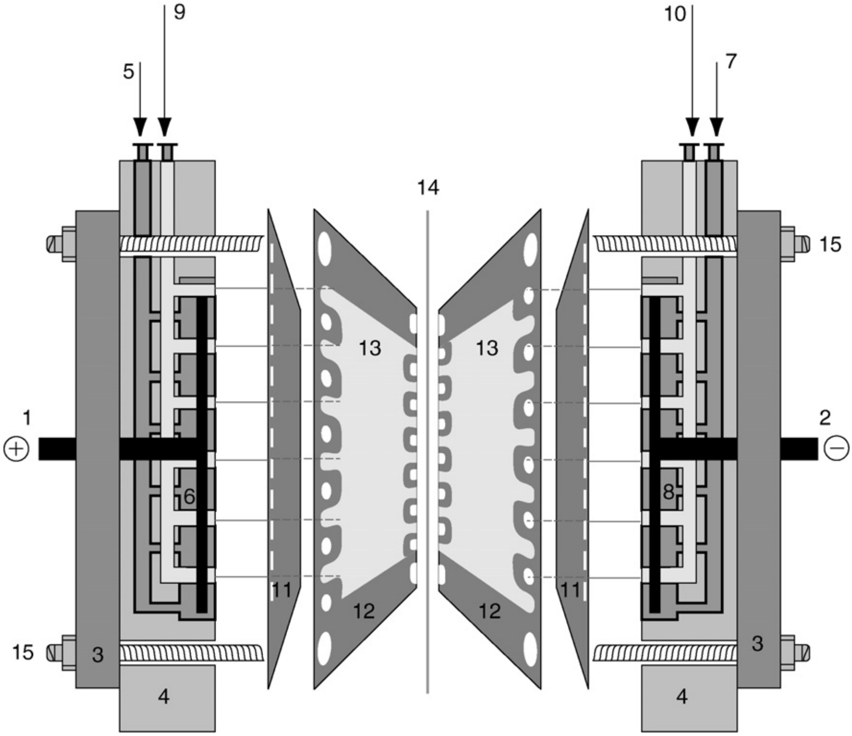


FIG. 4 Exploded view of an ED stack with indications of its main items: 1, anode; 2, cathode; 3, steel frame; 4, plastic end plate; 5, inlet anode compartment; 6, anode chamber; 7, inlet cathode compartment; 8, cathode chamber; 9, inlet-concentrating compartment; 10, inlet-diluting compartment; 11, cation-exchange membrane; 12, spacer-sealing frame; 13, spacer net; 14, anion-exchange membrane; 15, screws.

stack components together. The inside surfaces of the electrodes, generally consisting of carbon, stainless steel, or titanium, are recessed (Figure 4) so as to form an electrode-rinse compartment when an IEM or a neutral one is clamped in place.

The basic unit of an ED stack is the so-called *cell pair*, which consists of a couple of anionic and cationic membranes together with their adjacent compartments (Figure 5A). By applying a direct electric voltage to the electrodes, the ions in the solution flowing in a generic compartment tend to migrate toward the electrode with opposite charge. Cations freely flow through the cationic membranes, but they are retained by the anionic ones. On the contrary, anions can permeate across the anionic membranes, while they are rejected by the cationic ones. The overall result of this process is that

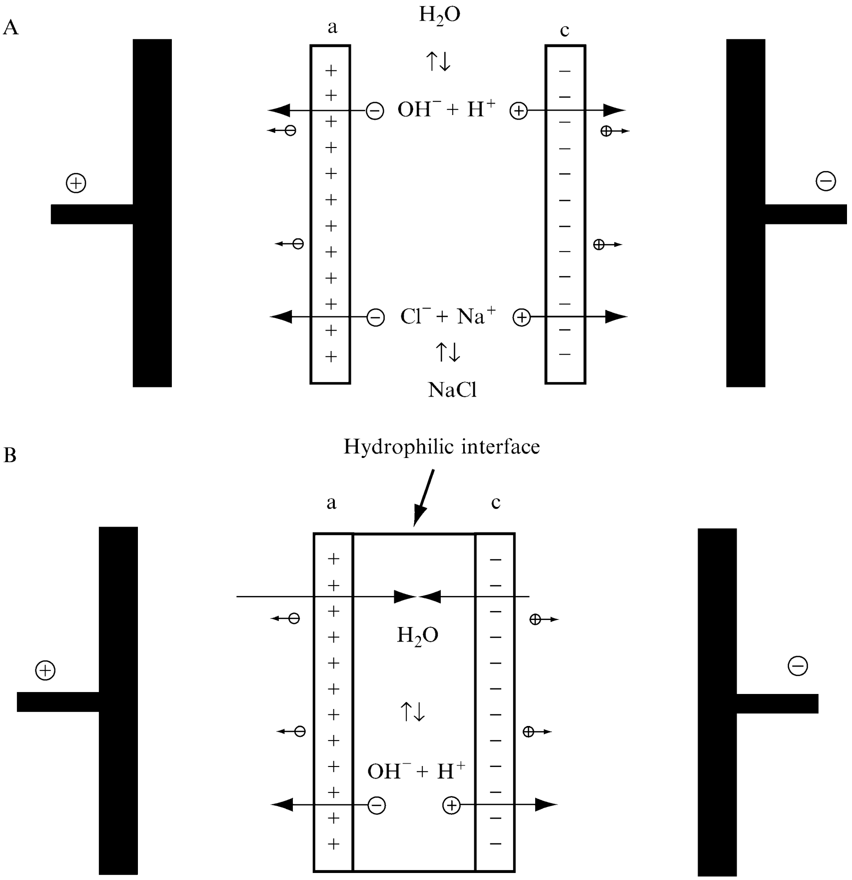


FIG. 5 Basic operating principles of an electrodialysis process using (A) a couple of monopolar (anionic, a, and cationic, c) membranes or (B) a bipolar membrane.

the electrolyte concentration increases in a series of alternate (e.g., *concentrating*) compartments and simultaneously decreases in the other adjacent (e.g., *diluting*) compartments.

The number of cell pairs can vary up to 1000 in commercial units. For instance, the stack EUR40 commercialized by Eurodia Industrie (Wissous, F) can assemble up to 1000 cells using various intermediate plates with and without electrodes, each cell pair having an effective membrane surface area of 0.4 m^2. Pilot-scale units, such as EUR2 or EUR6, may contain up to 10 or 80 cells with a surface area of 0.02 or 0.06 m^2, respectively (htpp://www.eurodia.com).

The usual thickness of commercial membranes ranges from 0.05 to 0.8 mm (Table II), while each channel gap is of a few millimetres. The thinner the membrane, the smaller the electric resistance and mechanical strength become, whereas the narrower the channels, the greater their conductance and pressure drops are.

ED stacks can be subdivided into two basic types: tortuous path or sheet flow (Figure 6). In the former, the solution is forced at superficial velocities (v_S) of 30–50 cm/s through a long (about 100 times the nominal membrane width) narrow channel with numerous 180° bends between the inlet and outlet ports of a compartment and a great number of cross-straps to support the membrane itself and promote turbulence in the flowing solution (Figure 6A). On the contrary, in the latter the solution approximately flows along the straight line linking the entrance and exit ports of any compartment (Figure 6B) at quite smaller v_S values (5–15 cm/s).

The differences in v_S, direction changes, and path length make the pressure drop (200–400 kPa) through a tortuous-path stack by far greater than that (20–70 kPa) in a sheet-flow one, as reported by Lacey (1972) and Strathmann (1992).

In tortuous-path stacks there is no need for spacer screens as thicker membranes, narrow channels, and plenty of cross-straps are used. On the contrary, in sheet-flow stacks spacers of different geometry and thickness are necessary to prevent membrane contact (that would result in burning through), as well as to induce turbulence in the flowing solution (Kuroda *et al.*, 1983). Spacers generally consist of a sealing frame and a net in the

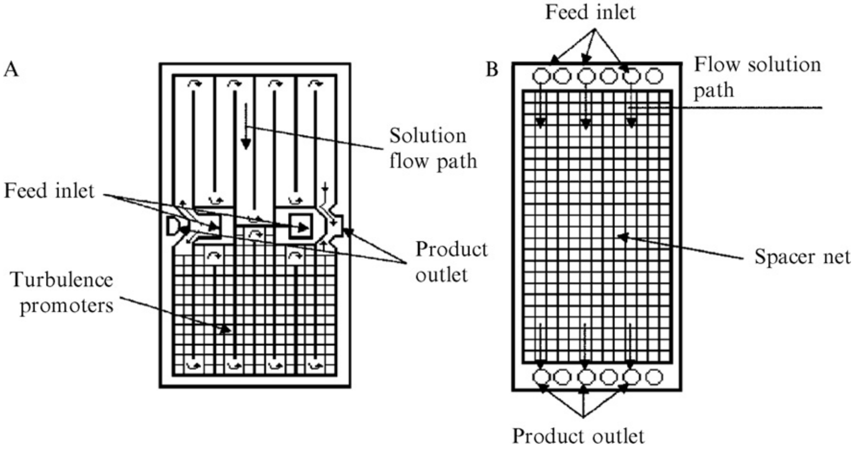


FIG. 6 Schematic diagrams of (A) tortuous-path and (B) sheet-flow ED spacer gaskets.

active area, which is filled with the electrolyte. Once the spacers have been stacked, the openings in the sealing frame result in tubes, which are arranged so as to build both the channel systems for the concentrating and diluting streams (Figure 6).

Whereas the tortuous path stacks are manufactured by Ionics Inc. (Watertown, MA, US) (http://www.ionics.com) only, the sheet-flow ones are produced by several companies, such as Astom Co. (Minato-Ku, Tokyo, Japan; http://www.astom-corp.jp), a jointed company of Tokuyama Co. (Shibuya-ku, Tokyo, Japan) and Asahi Chemical Industry Co. (Chiyoda-ku, Tokyo, Japan) founded in 1995; Asahi Glass Engineering Co. (Chiyoda-ku, Tokyo, Japan; http://www.agc.co.jp/english/chemicals/ion-maku/selemion/sele.htm#anchor795659); Du Pont Co. (Fayetteville, NC, US; http://www.dupont.com/fuelcells/pdf/nae101.pdf); Electropure Excellion™ (Laguna Hills, CA, US; http://www.electropure-inc.com/downloads/Excellion%20Specifications.pdf); Linan Euro-China Co. (Linan City, China; http://www.Linanwindow.Com/Qianqiu/Membeng.Htm); Membranes International Inc. (Glen Rock, NJ, US; http://www.membranesinternational.com/tech.htm); Pall RAI Inc. (Hauppauge, NY, US); PCA GmbH (Heusweiler, D; http://www.pca-gmbh.com); Permutit Co. (UK), that became a part of the USFilter Corp. (Warrendale, PA, US; http://www.usfilter.com/water/Business+Centers/Industrial_Process_Water/Industrial_Process_Water_Products/pw_permutit.htm) in 1993; Rhone-Poulenc Chemie GmbH (Frankfurt, D); and Sybron Chemicals Inc. (Birmingham, NJ, US; http://www.ion-exchange.com/products/membranes/index.html).

b. ED stack arrangement. Depending on the peculiar application, several arrangements of ED stacks are used. The simplest case, that is, the *batch desalination process*, is carried out by circulating the solution through the stack from a storage vessel and vice versa (Figure 7A) until the desired degree of ion depletion or enrichment is achieved, this being characterized by specific target values for the electric conductivity of the dilute and/or concentrate. As the electric conductivity of the dilute reduces, the voltage potential applied to the ED stack has to be increased to keep the current density constant, thus raising the overall electric energy consumption.

It is also possible to run an ED process in the *continuous* mode (Figure 7B) by letting simultaneously a fresh feed enter the ED unit and the final product flow out of it. This operation can be performed in one or more than one turn. The latter is generally referred to as the *feed-and-bleed* mode (Figure 7C) and needs a portion of the product to be blended with the raw inlet feed solution. This procedure is applied when the feed solute concentration fluctuates and a continuous flow of product is required or when the demineralization degree is low. To minimize the overall membrane

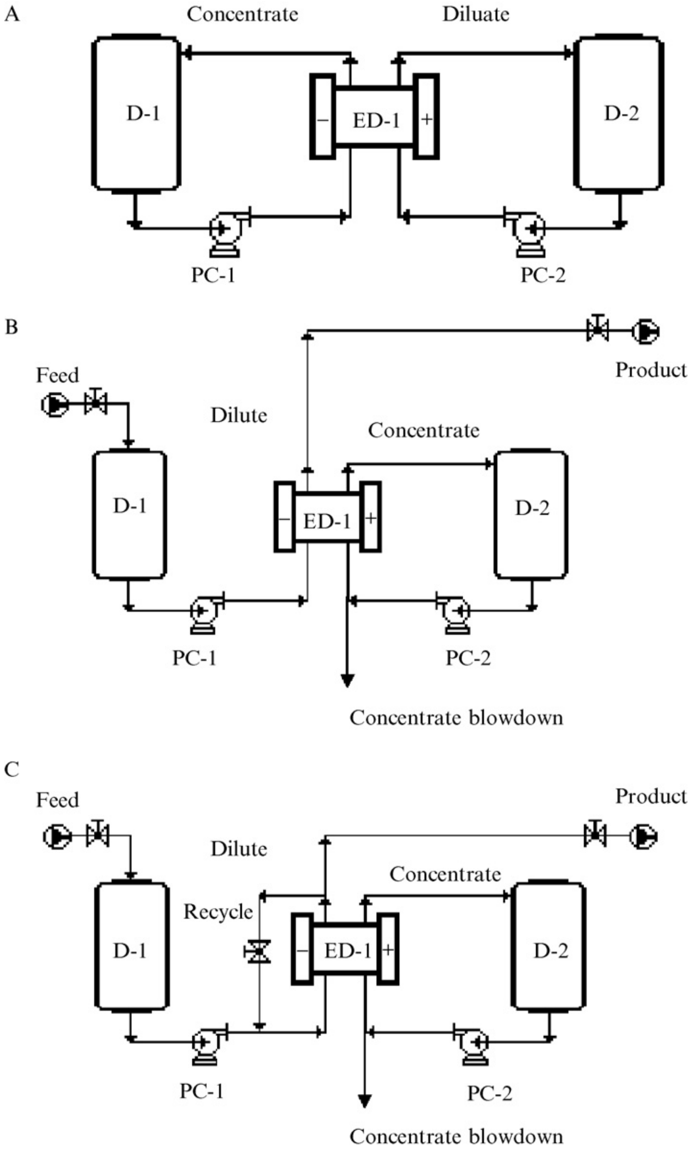


FIG. 7 Flow diagrams of the different operating modes for an ED unit: (A) batch process; (B) continuous single-passage process; and (C) feed-and-bleed process.

surface area installed, the de-ashing process can be fractionated into several feed-and-bleed stages, arranged in series and operated at progressively smaller current densities.

In the continuous mode, scaling of carbonates and hydroxides may be prevented by resorting to automatic acid addition to control the pH of the concentrate or to periodic or continuous concentrate blowdown.

Whatever the operating mode, an ED unit can work with constant polarity (that is in the conventional or unidirectional ED) or with reversed polarity. The latter was first proposed by Ionics Inc. (Watertown, MA, US) in the early 1970s (http://www.ionics.com/products/membrane/WaterDesalting/edr/edr2020.htm) as the *ED reversal process* (EDR) to solve one of the problems encountered in water desalination processes, that is, membrane fouling or scaling as due to the organic or inorganic substances present in brackish water. This process consists of inverting the polarities of the electrodes periodically (i.e., at time intervals varying from a few minutes to several hours), as well as the hydraulic flow streams. In the circumstances, fouling or scaling constituents that build up especially on the anionic membrane surfaces of the concentrating compartments in one cycle are removed or redissolved in the next cycle, when the concentrating compartments are reverted to the diluting ones. For instance, in the new Ionics EDR 2020 system the polarity of the DC power is reversed from two to four times per hour so as to allow automatic self-cleaning of membrane surfaces.

For more than 30 years, the EDR mode has been the process of choice in the desalination industry. It is today applied in other ED applications (e.g., whey demineralization) by other companies too (http://www.ameridia.com).

2. *Bipolar membranes*

At the end of the 1980s a new type of electromembrane (e.g., the bipolar membrane, bpm) started to be commercialized (Bazinet *et al.*, 1998). It consists of an anion- and a cation-exchange membrane that are bound together, either physically or chemically, and of a very thin hydrophilic layer (< 5 nm), where water molecules diffuse from the outside aqueous salt solutions (Figure 5B). In the presence of an electrical field, these molecules are dissociated into hydrogen (H^+) and hydroxyl (OH^-) ions (Mani, 1991). These ions can migrate out of that layer, provided that the bipolar membrane is correctly oriented (no current reversal being allowed in water splitting). With the anion-exchange side facing the anode and the cation-exchange side facing the cathode, the hydroxyl anions will flow across the anion-exchange layer and the hydrogen cations across the cation-exchange layer. In the circumstances, bipolar membranes allow an efficient generation and concentration (up to 10 kmol/m^3) of hydroxyl and hydrogen ions at their surfaces, thus resulting in the production of basic and acidic solutions, respectively.

The main advantages of bipolar membranes are no formation of gases at their surfaces or within the bipolar membranes themselves, a power consumption to dissociate water into O_2 and H_2 about half that used in electrolytic cells, a minimum formation of by-product or waste streams in the case of dilute (< 1 kmol/m^3) acids or bases, and reduced downstream purification steps.

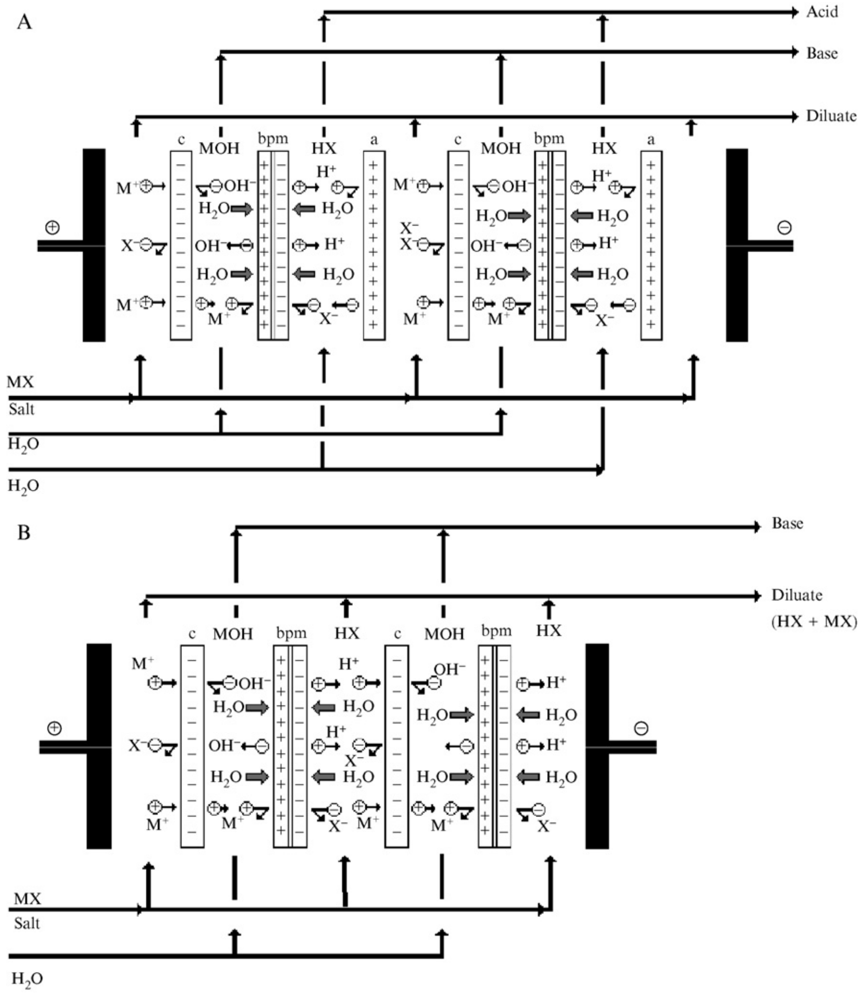
The requirements for a bipolar membrane are low electrical resistance at high current density, high water dissociation rates, low co-ions transport rates, high ion selectivity, and good chemical and thermal stability in strong acids and bases. Low electrical resistance of the cationic and anionic layers of bpms can be obtained by using, for instance, sulphonic acid groups in the cation-exchange layer and quaternary amines in the anion-exchange layer of the bipolar membranes as fixed charges at high concentrations in the polymer matrix.

Tokuyama Soda Co. Ltd. (www.tokuyama.co.jp), the main shareholder of Eurodia Industries (http://www.eurodia.com), has developed a bipolar membrane type BP-1E, that is characterized by a thickness of 0.2–0.35 mm, a burst strength of 0.4–0.7 MPa, and water-splitting voltage and efficiency of 1.2–2.2 V and 98%, respectively (http://phychem.kjist.ac.kr/312.pdf). Other bpms with quite similar characteristics (http://www.hansei.com/filtra/ion-b2.htm; http://phychem.kjist.ac.kr/312.pdf) are manufactured by Aqualytics Inc. (Warren, NJ, USA), that has been acquired by FuMA-Tech GmbH (St. Ingbert, D; http://www.fumatech.com/).

a. ED stack arrangement. ED stacks using bpms can be arranged in two or three compartments and operated in a single- or multipassage continuous or batch mode as any conventional ED stack. The most common three-compartment configuration, obtained by interposing a bpm between an anionic (a) and a cationic (c) membrane, is used to split a salt solution into an acidic and a basic stream, each flowing out of the compartments limited by a bipolar and an anionic membrane and by a bipolar and a cationic membrane, respectively (Figure 8A). In this configuration, it is possible to arrange up to 200 cells in a single stack provided with a system of manifolds suitable to feed the three corresponding compartments in parallel, that is, acid, base, and dilute, besides the two electrode compartments.

By feeding a salt solution into the diluting compartments and water into both acid and base compartments, and by supplying a DC across the electrodes, it is possible to split a salt of an organic acid into the free acid and the corresponding hydroxide. In this process, only a small percentage (1–2%) of the overall power is consumed at the electrodes where small amounts of hydrogen and oxygen are generated.

In the two-compartment configuration, it is possible to couple a bpm with a cation- or an anion-exchange membrane only, thus minimizing both the overall investment and operating costs for the ED unit needs one less process loop, less membranes to install and replace and, consequently, less power to operate under constant-current density.



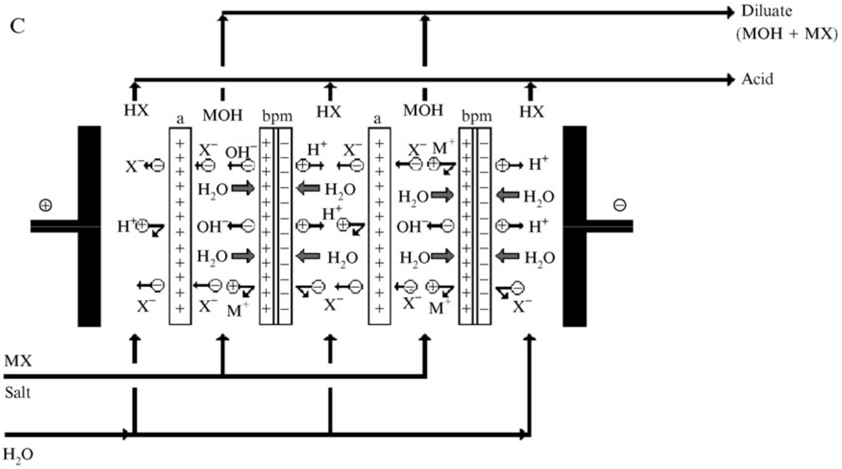


FIG. 8 Schematic diagrams of different arrangements for an ED unit equipped with bipolar membranes (bmp) coupled to anionic (a) and/or cationic (c) membranes: (A) three-compartment configuration; (B) two-compartment configuration using bipolar and cationic membranes; (C) two-compartment configuration using bipolar and anionic membranes.

The two-compartment cells made of bipolar and cation- or anion-exchange membranes (Figure 8B and C) are useful to convert a salt of a weak acid and a strong base (such as the sodium salts of acetic, lactic, and formic acids, or sodium glycinate) or a weak base and a strong acid (such as ammonium chloride or sulfate) into a concentrated stream containing the corresponding strong base (Figure 8B) or acid (Figure 8C) and a diluting stream containing the residual fraction of the salt (e.g., 1–2% w/w) together with its corresponding free weak acid (Figure 8B) or base (Figure 8C). In these cases, it is impractical to use the three-compartment cell owing to poor electric conductivity of the corresponding weakly dissociated acid or base.

Over the last 15 years, about 2500 m^2 of bpms have been installed throughout the world to produce specialty and fine chemicals, such as amino and organic acids (Gillery *et al.*, 2002). A successful operation of an ED unit using bpms depends on several factors, such as a feed multivalent cation content not greater than 1–5 g/m^3 to avoid their precipitation over the cation-exchange membranes as they react with hydroxyls in the stack, a salt concentration greater than 1 $kmol/m^3$ to operate at high current density and reduce the membrane area required, an oxidizing compound-free feed, and a maximum operating temperature smaller than 40 °C (Gillery *et al.*, 2002).

C. MASS TRANSFER IN AN ED STACK

Despite there is not yet enough knowledge on the exact phenomena taking place in the electromembranes, the ion flux in a generic electromembrane can, for the sake of simplicity, be described by means of an expression analogous to Eq. 6, where the ion transport number in solution ($t^{\pm}$) is replaced with that in the membrane phase ($t_{\mathrm{m}}^{\pm}$). Owing to the charged groups chemically attached to their support matrix, anionic or cationic membranes allow intrusion and exchange of negative or positive ions from an external source, as well as exclusion of the cations or anions, respectively (Figure 5). Thus, the transport number for anions in anion-exchange membranes would tend to 1, while that for cations to zero and vice versa for a cation-exchange membrane.

The anionic or cationic membrane perm-selectivity (α_{m}) for the corresponding counterions can be expressed as the ratio by the differences between the real and theoretical transport numbers in the membrane and solution phases:

$$\alpha_{\mathrm{m}} = \frac{t_{\mathrm{m}}^{\pm} - t^{\pm}}{1 - t^{\pm}} \tag{10}$$

When the counterion transport number in the membrane is the same as in the electrolytic solution, the perm-selectivity tends to zero (Strathmann, 1992).

As a result of the different ionic mobility in the solution and membrane phase, some species are rejected and, therefore, accumulate at one side of a semipermeable barrier, producing a concentration gradient and the so-called phenomenon of *concentration polarization* (CP). For instance, in the case of the flux of Cl^{-} in an ED stack, the transport numbers in the anionic membrane (t_{a}^{-}) and bulk solution (t^{-}) are about unitary and 0.6, respectively. This means that the capacity of the anionic membrane to convey Cl^{-} is greater than that of the concentrated solution, thus making the side of the anionic membrane facing the concentrated stream richer in Cl^{-}. Similarly, at that side there is also accumulation of Na^{+} since the transport number for Na^{+} in solution ($t^{+} \approx 0.4$) is greater than that in the anionic membrane ($t_{\mathrm{a}}^{+} \approx 0$). On the other side of the anionic membrane facing the diluting stream, the flux of Cl^{-} is greater in the membrane than in the bulk solution, thus making the membrane surface depleted of Cl^{-}.

Figure 9 shows a schematic diagram of an ED unit with the simplified concentration profiles in an ED cell pair.

In agreement with the great majority of the authors involved in ED stack design and optimization (Bailly *et al.*, 2001; Boniardi *et al.*, 1996, 1997; Fidaleo and Moresi, 2005a; Ibanez *et al.*, 2004; Lee *et al.*, 1998, 2002d; Nikonenko *et al.*, 2002, 2003; Yen and Cheryan, 1993), the overall ion flux

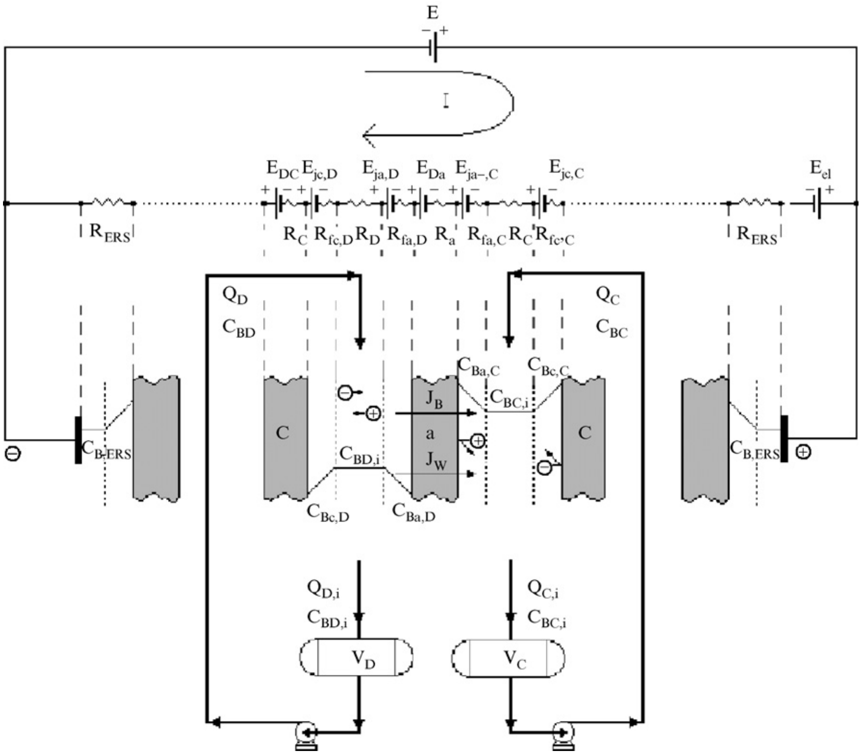


FIG. 9 Flow diagram for an ED unit together with the simplified concentration profiles in an ED cell pair and the analogous electrical circuit. All symbols are defined under the heading "Abbreviations".

in an ED cell pair was described using the Nernst–Planck (NP) equation that contains two terms expressing the contribution of diffusion and electromigration in the ionic transport (Buck, 1984) and can be regarded as a reduced form of the Maxwell-Stefan (MS) equation in the case of dilute systems (Krishna, 1987; Krishna and Wesselingh, 1997). In this way, only one diffusion coefficient per ionic species in each phase is necessary and this simplicity allows such equation to be easily coupled to other equations describing hydrodynamic conditions, water transport through the electromembranes, chemical reactions in the solutions and membrane, boundary, and other conditions. Even if such oversimplification should restrict the applications of NP equation for salt concentrations below 0.1 kmol/m^3 (Krishna, 1987), NP-based models were used to describe the ED desalination performance up to feed sodium chloride concentrations of 0.5 kmol/m^3

(Lee *et al.*, 2002d) or up to 1.7 kmol/m^3 (Fidaleo and Moresi, 2005a) provided that the model parameters were estimated using existing correlations or determined by independent experiments, respectively.

For the ED cell pair sketched in Figure 9, the overall flux of solute will be:

$$J_{\mathrm{B}} = \frac{t_{\mathrm{s}}}{F}\, j - L_{\mathrm{B}} \Delta c_{\mathrm{B}} \tag{11}$$

where L_{B} is the membrane constant for solute transport by diffusion, t_{s} is the effective cation ($= t_{\mathrm{c}}{}^{+} - t_{\mathrm{a}}{}^{+}$) or anion ($= t_{\mathrm{a}}{}^{-} - t_{\mathrm{c}}{}^{-}$) transport number, while Δc_{B} ($= c_{\mathrm{BC}} - c_{\mathrm{BD}}$) is the difference in solute concentrations in C and D compartments, provided that the polarization effect is negligible. The negative sign at the right hand side of Eq. 11 accounts for the reverse direction of solute diffusion with respect to ion electromigration.

In the same ED cell pair, the overall water transport through the electromembranes from the dilute stream to the concentrate one can be expressed by accounting for electroosmosis (i.e., the migration of water molecules associated with ions, this being proportional to j) and osmosis phenomena:

$$J_{\mathrm{W}} = \frac{t_{\mathrm{W}}}{F}\, j + J_{\mathrm{Wd}} \tag{12}$$

In accordance with the Spiegler-Kedem model (Krishna and Wesselingh, 1997), J_{Wd} is proportional to the net pressure difference across the membranes. Since the pressure difference (ΔP) may be regarded as negligible, J_{Wd} is mainly controlled by the corresponding instantaneous osmotic pressure difference ($\Delta\pi$), this being proportional to the difference in solute concentration across the membranes for a great number of solutes (Lo Presti and Moresi, 2000):

$$J_{\mathrm{Wd}} = L_{\mathrm{p}}(\sigma \Delta\pi - \Delta P) \approx L_{\mathrm{p}} \sigma \Delta\pi \approx L_{\mathrm{W}} \Delta c_{\mathrm{B}} \tag{13}$$

where L_{W} is the membrane constant for water transport by diffusion.

1. Limiting current concept

With reference to Figure 9, at the boundary layers adjacent each electromembrane in the diluting or concentrating compartment it is possible to establish the following ion mass balance by accounting for the ion transport corresponding to NP equation both in solution and membrane phases:

$$J^{\pm} = \frac{t^{\pm}}{z^{\pm}} \frac{j}{F} - D_{\mathrm{B}} \frac{\mathrm{d}c^{\pm}}{\mathrm{d}x} = \frac{t^{\pm}_{\mathrm{m}}}{z^{\pm}} \frac{j}{F} \tag{14}$$

Upon integration over the generic boundary layer of thickness δ, in the case of a monovalent electrolyte, it follows:

$$j = \frac{k_m F(c_{Bk} - c_{Bmk})}{t_m^{\pm} - t^{\pm}} \tag{15}$$

where k_m is the mass transfer coefficient ($= D_B/\delta$), c_{Bk} and c_{Bmk} are the solute molar concentrations in the bulk solution in compartment k and at the generic membrane surface.

The so-called *limiting current density* is the first value at which current density is diffusion limited (Cowan and Brown, 1959), that is, the value at which the electrolyte concentration at any membrane surface falls to zero:

$$j_{\mathrm{lim,c}} = \frac{F c_{BD} k_m}{(t_c^+ - t^+)}; \quad j_{\mathrm{lim,a}} = \frac{F c_{BD} k_m}{(t_a^- - t^-)} \tag{16}$$

where c_{BD} is the bulk solute concentration in the dilute solution.

Equation 16 assumes that a concentration gradient exists only in the direction perpendicular to the membrane surface, that is, the flow pattern in the cell is turbulent in such a way that vertical concentration gradients are eliminated, as observed using a tracer dye by Krol *et al.* (1999).

As shown by Eq. 16, $j_{\mathrm{lim,k}}$ should vary linearly with c_{BD} and increase as k_m increases.

2. *Mass transfer coefficient*

As shown in Table III, several authors (Fidaleo and Moresi, 2005a; Kraaijeveld *et al.*, 1995; Kuroda *et al.*, 1983; Sonin and Isaacson, 1974) established power function relationships between the Sherwood number (*Sh*) and the Reynolds (*Re*) and Schmidt (*Sc*) numbers in ED cells equipped with different eddy promoters, even if different definitions of the equivalent diameter were used to calculate the Reynolds number.

In a great number of papers dealing with the design of ED stacks, and especially in the recent and comprehensive paper by Lee *et al.* (2002d), the solute mass transfer coefficient (k_m) is expressed as a nonlinear function of the superficial flow velocity (v_S):

$$k_m = \alpha_0 v_S^{\alpha_1} \tag{17}$$

where α_0 and α_1 are empirical coefficients depending on the cell and spacer construction with α_1 ranging from 0.5 to 1.

One of the main disadvantages of the above-mentioned relationship is that it does not account for the variation of density (ρ), viscosity (η), and solute diffusivity (D_B) with c_B. On the contrary, the use of dimensionless *Sh*, *Re*, and *Sc* numbers has been traditionally regarded as the most accurate mode to deal with such variations. The empirical dimensionless correlations reported in Table III, except for the one established by Kraaijeveld *et al.* (1995),

TABLE III

EMPIRICAL CORRELATION FOR PREDICTING THE SOLUTE MASS TRANSFER COEFFICIENT (k_m) IN ED CELLS WITH EDDY PROMOTERS

	Re		d_e	References
Correlation	Definition	Range	(mm)	
$Sh = 0.43\mathrm{Re}^{1/2}Sc^{1/3}\sqrt{\dfrac{d_e}{d_{eR}}}$	$Re = \dfrac{\rho v_S d_e}{\eta(1-\varepsilon_S)}$	50–70	$d_e = 3.7–4.2$	Kuroda *et al.*, 1983
	$d_e = \dfrac{2hW(1-\varepsilon_S)}{h+W}$		$d_{eR} = 1.58$	
$Sh = 1.9Re^{1/2}Sc^{1/3}\sqrt{\dfrac{h}{\Delta l}}$	$Re = \dfrac{\rho v_S h}{\eta}$	300–2000	–	Sonin and Isaacson, 1974
$Sh = 8.09Re^{0.13}Sc^{1/3}\sqrt{\dfrac{h}{\Delta l}}$	$Re = \dfrac{\rho v_S h}{\eta}$	100–300	–	Kraaijeveld *et al.*, 1995
$Sh = (0.53 \pm 0.01)Re^{1/2}Sc^{1/3}$	$Re = \dfrac{\rho v_S h}{\eta}$	10–25	–	Fidaleo and Moresi, 2005a

show that k_m is proportional to the square root of v_S, this being in agreement with the average experimental value (0.47 ± 0.05) obtained by Lee *et al.* (2002d).

For instance, by using the correlations previously developed as referred to an ED cell, equipped with AMV or CMV membranes (Table II) and 0.4-mm thick spacers, it was possible to estimate that, as NaCl concentration increased from 0 to 2 kmol/m^3, D_B was of the order of 1.2×10^{-9} m^2/s, the *Sh* was practically constant and equal to about 22, and k_m ranged from 53 to 77 μm/s (Fidaleo and Moresi, 2005a).

D. OVERALL POTENTIAL DROP ACROSS AN ED STACK

Anytime a generic boundary layer or semipermeable barrier separates two phases or zones at different electrolyte concentrations a junction (E_j) or a Donnan (E_D) potential is established, the value of which can be estimated in accordance with Boniardi *et al.* (1996), Prentice (1991), and Vetter (1967).

By referring to Figure 9, in any cell pair the presence of an anionic and a cationic membrane gives rise to four boundary layers and thus to four junction potentials differences ($E_{ja,k}$ and $E_{jc,k}$) and two Donnan potential differences (E_{Da} and E_{Dc}), their mathematical expressions being given in Table IV.

In the equivalent electrical circuit of the ED stack sketched in Figure 9, such potentials were regarded as a series of batteries the polarities of which were *a priori* assumed as coincident with those of the external DC generator (E), except for the DC generator representing the thermodynamic and overpotential of electrodes (E_{el}). For instance, since $t_a^- > t_a^+$ and $c_{Ba,D}$ is generally smaller than $c_{Ba,C}$, E_{Da} is negative. Thus, it should be represented as a DC generator with inverted polarities with respect to that sketched in Figure 9. By contrast, in the case of $t^- > t^+$, since $c_{Ba,C}$ is generally greater than c_{BC}, $E_{ja,C}$ is positive, thus being equivalent to a DC generator with the same polarities of the external DC generator, that is, as the corresponding DC generator shown in Figure 9.

To estimate E_j and E_D, it is necessary to estimate the electrolyte concentrations at the membrane surfaces. On the assumption that the boundary layers established are invariant, such concentrations can be calculated on the basis of the bulk concentrations, current density, transport number of ions, and mass transfer coefficient (k_m), via Eq. 15.

By applying the second Kirchhoff's law to the equivalent electrical circuit of the ED stack (Figure 9), the overall potential drop across an ED stack can be written as:

$$E - E_{el} + (E_j + E_D)N_{cell} = RI \qquad (18)$$

TABLE IV

MATHEMATICAL EXPRESSIONS OF THE JUNCTIONS ($E_{\mathrm{ja,k}}$ AND $E_{\mathrm{jc,k}}$) AND DONNAN (E_{Da} AND E_{Dc}) POTENTIAL DIFFERENCES FOR A GENERIC ANIONIC OR CATIONIC MEMBRANE; RESISTANCES OF THE BOUNDARY LAYERS ADJACENT TO THE ANIONIC ($R_{\mathrm{fa,k}}$) AND CATIONIC ($R_{\mathrm{fc,k}}$) MEMBRANES, OF BULK SOLUTIONS (R_{k}) IN D AND C COMPARTMENTS, AND ELECTRODE-RINSING SOLUTION (R_{ERS})[a]

Parameter	C compartment	D compartment
$E_{\mathrm{ja,k}}$	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t^{-}-t^{+})\ln\left(\dfrac{c_{\mathrm{Ba,C}}}{c_{\mathrm{BC}}}\right)$	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t^{-}-t^{+})\ln\left(\dfrac{c_{\mathrm{BD}}}{c_{\mathrm{Ba,D}}}\right)$
$E_{\mathrm{jc,k}}$	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t^{-}-t^{+})\ln\left(\dfrac{c_{\mathrm{BC}}}{c_{\mathrm{Bc,C}}}\right)$	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t^{-}-t^{+})\ln\left(\dfrac{c_{\mathrm{Bc,D}}}{c_{\mathrm{BD}}}\right)$
E_{Da}	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t_{a}^{-}-t_{a}^{+})\ln\left(\dfrac{c_{\mathrm{Ba,D}}}{c_{\mathrm{Ba,C}}}\right)$	
E_{Dc}	$\dfrac{R_{\mathrm{G}}T_{\mathrm{K}}}{F}(t_{c}^{+}-t_{c}^{-})\ln\left(\dfrac{c_{\mathrm{Bc,D}}}{c_{\mathrm{Bc,C}}}\right)$	
$R_{\mathrm{fc,k}}$	$\dfrac{2D_{\mathrm{B}}F}{ja_{\mathrm{me}}\Lambda_{0}(t_{\mathrm{c}}^{+}-t^{+})}\ln\left[\left(\dfrac{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{BC}}}}{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{Bc,C}}}}\right)\left(\dfrac{\sqrt{c_{\mathrm{Bc,C}}}}{\sqrt{c_{\mathrm{BC}}}}\right)\right]$	$\dfrac{2D_{\mathrm{B}}F}{ja_{\mathrm{me}}\Lambda_{0}(t_{\mathrm{c}}^{+}-t^{+})}\ln\left[\left(\dfrac{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{Bc,D}}}}{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{BD}}}}\right)\left(\dfrac{\sqrt{c_{\mathrm{BD}}}}{\sqrt{c_{\mathrm{Bc,D}}}}\right)\right]$
$R_{\mathrm{fa,k}}$	$\dfrac{2D_{\mathrm{B}}F}{ja_{\mathrm{me}}\Lambda_{0}(t_{\mathrm{a}}^{-}-t^{-})}\ln\left[\left(\dfrac{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{BC}}}}{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{Ba,C}}}}\right)\left(\dfrac{\sqrt{c_{\mathrm{Ba,C}}}}{\sqrt{c_{\mathrm{BC}}}}\right)\right]$	$\dfrac{2D_{\mathrm{B}}F}{ja_{\mathrm{me}}\Lambda_{0}(t_{\mathrm{a}}^{-}-t^{-})}\ln\left[\left(\dfrac{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{Ba,D}}}}{\Lambda_{0}+\beta_{1}\sqrt{c_{\mathrm{BD}}}}\right)\left(\dfrac{\sqrt{c_{\mathrm{BD}}}}{\sqrt{c_{\mathrm{Ba,D}}}}\right)\right]$
R_{k}	$\dfrac{h-2\delta}{a_{\mathrm{me}}c_{\mathrm{BC}}\Lambda(c_{\mathrm{BC}})}$	$\dfrac{h-2\delta}{a_{\mathrm{me}}c_{\mathrm{BD}}\Lambda(c_{\mathrm{BD}})}$
R_{ERS}	$\dfrac{h_{\mathrm{ERS}}}{a_{\mathrm{ERS}}c_{\mathrm{B,ERS}}\Lambda(c_{\mathrm{B,ERS}})}$	

[a] As extracted from Fidaleo and Moresi (2005a).

where I is the current flowing through the ED device; E_{el} the electrode potentials for anode and cathode processes; R the overall resistance of the membranes, bulk solutions, boundary layers, and electrode-rinsing solutions; E_{j} and E_{D} are the overall junction and Donnan potential differences across the boundary layers and membranes pertaining to any cell, respectively; and N_{cell} the overall number of cells, each one being composed of a couple of anionic and cationic membranes.

The overall electric resistance of the ED stack can be expressed as follows:

$$R = (R_{\mathrm{c}} + R_{\mathrm{fc,D}} + R_{\mathrm{D}} + R_{\mathrm{fa,D}} + R_{\mathrm{a}} + R_{\mathrm{fa,C}} + R_{\mathrm{C}} + R_{\mathrm{fc,C}})N_{\mathrm{cell}} + 2R_{\mathrm{ERS}} \tag{19}$$

where $R_{\mathrm{fa,k}}$ and $R_{\mathrm{fc,k}}$ are the resistances of the boundary layers adjacent to the anionic and cationic membranes in the generic k-th compartment, R_{c} and R_{a}, R_{C} and R_{D}, and R_{ERS} are the resistances of the cationic and anionic membranes, the bulk solution in C and D compartments, and electrode-rinsing solution, respectively.

Except the membrane resistances, any other generic k-th ohmic resistance can be estimated by applying the second Ohm's law:

$$R_{\mathrm{k}} = \int_0^s \frac{\mathrm{d}x}{\chi a_{\mathrm{k}}} \tag{20}$$

where a_{k} is the effective membrane or electrode surface area involved in the ion flow pattern, while χ and s are the electric conductivity and thickness of the electrolyte solution involved.

Table IV also reports the mathematical expressions useful to estimate such resistances, where the electric conductivity of the solutions involved was expressed in terms of equivalent conductance. For the sake of simplicity, the resistances of the boundary layers adjacent to any membrane were estimated by expressing the equivalent conductance as a linear function of the square root of solute concentration, that is, by neglecting the contribution of the empirical coefficients β_2 and β_3 of Eq. 4.

When recirculating the same electrolytic solution through the concentrating and diluting compartments of an ED cell while increasing the voltage applied by the external DC generator, it is possible to establish a characteristic current–voltage relationship. For $E < E_{\mathrm{d}}$ negligible current flows through the cell, while for $E > E_{\mathrm{d}}$ the current starts to increase with E, thus exhibiting a typical three-region pattern. In the first region (the so-called *ohmic region*) a linear relationship is observed. As E increases, the solute concentration at the membrane surface reduces. As c_{B} falls to zero, a first deviation in the linear trend of the E versus I plot is observed. Any further increase in E gives rise to a smaller increase in I, thus leading to the

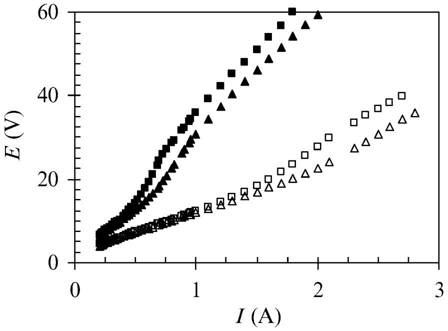


FIG. 10 Main results of typical limiting current tests performed using a membrane pack composed of 19 CMV membranes (Table II) under two levels of NaCl concentration ($c_B = 9$ mol/m^3, closed symbols; $c_B = 28$ mol/m^3, open symbols) and superficial velocity v_s (□, ■: 3.4 cm/s; △, ▲: 5.9 cm/s), as derived from Fidaleo and Moresi (2005a): voltage (E) vs. current intensity (I).

second region (sometimes called *plateau region*) (Krol *et al.*, 1999). By continuing to increase E, I tends to increase again, thus allowing the presence of the third over-limiting region to be revealed. In conventional ED stacks, polarization results in the following phenomena: as the limiting current is exceeded, the apparent resistance of the cell rises sharply, the pH of the dilute falls, while that of the concentrate increases, the Coulomb efficiency falls. Wen *et al.* (1996) demonstrated that the main mechanism responsible for all these phenomena is a large fall in the net electrical motive force (emf), mainly due to a great increase in the back emf, due to the membrane concentration potential, while the increase in the real ohmic resistance of the stack was minimal as the contribution of water dissociation was negligible, ranging from 1% (Wen *et al.*, 1996) to 3% (Krol *et al.*, 1999).

Both the first (ohmic) and second (polarization controlled) regions can be noted in Figure 10, reporting the results of typical limiting current measurements performed on an ED stack composed of only 19 cationic membranes (CMV type, see Table II) and model solutions containing 9 and 28 mol of NaCl per m^3 for superficial velocities (v_s) ranging from 3.4 to 5.9 cm/s (Fidaleo and Moresi, 2005a).

E. OVERALL ED PERFORMANCE INDICATORS

The major factors that determine the performance of an ED process are the solute recovery efficiency (ζ), total current efficiency (Ω), the specific energy consumption (ε), and the maximum solute weight concentration achievable in the concentrate ($C_{BC,max}$).

The solute recovery efficiency (ζ) is defined as the ratio between the solute mass (Δm_B) transported into the C stream or tank and the initial solute mass (m_{F0}) in the feed:

$$\zeta = \frac{\Delta m_B}{m_{F0}} \tag{21}$$

It can vary up to 95% depending on the application of choice and influences the overall energy consumption.

The total current efficiency (Ω) can be expressed as the product of two efficiencies:

$$\Omega = \Omega_C \Omega_L \tag{22}$$

where Ω_C is the Coulomb's efficiency and Ω_L is the current leakage efficiency. Whereas the former accounts for the imperfection of the electromembranes used, the latter for the inefficiency resulting from current leakage through pipes and manifolds. When the contribution of diffusion is negligible, Ω_C coincides with t_s. Since the co-ion transport numbers (t_a^+, t_c^-) in commercial electromembranes usually vary in the range 0.01–0.05, Ω_C is generally greater than 0.9. For instance, in ED stack equipped with AMV and CMV membranes (Table II) and treating aqueous solutions containing 12–37 kg of NaCl per m^3, t_s was 97 ± 2% in the constant-current region (Fidaleo and Moresi, 2005a). Thus, for well-designed laboratory-scale equipment and dilute solutions Ω is greater than 90%, while for commercial units it may reduce to about 50% (López Leiva, 1988).

The overall energy consumption (L) in an ED stack, as that sketched in Figure 9, can be calculated as:

$$L = \int_0^{\theta} E(\theta')I(\theta')\, d\theta' \tag{23}$$

where θ is the overall process time. When the operation is performed in the constant-current and -tension regions, L reduces to:

$$L = R_{MP} I^2 \theta \tag{24}$$

where R_{MP} is the overall apparent electric resistance of the ED stack.

The overall energy consumption per kilogram of solute recovered ($\varepsilon = L/\Delta m_B$) also accounts for the contributions of the thermodynamic potential and overpotential of electrodes ($E_{el}\, I$) and ohmic resistance of the electrode-rinsing solution ($R_{ERS}\, I^2$). However, such contributions are negligible in the industrial-scale ED stacks, that may be composed of 500–1000 cells. By neglecting such contributions, the specific energy consumption (ε) was found to increase from 0.18 (Fidaleo and Moresi, 2005a) to 0.22 (Fidaleo and Moresi, 2004) kWh/kg for a sodium chloride or lactate recovery yield (ζ) of 90% at 1 A and 20°C.

The water transport number (t_W) accounts for water transport associated to ion electromigration and thus controls the maximum solute weight concentration theoretically achievable in the concentrate. By dividing the instantaneous solute mass transferred into the C compartment by the actual volume accumulated into tank C for θ tending to infinite, the following can be obtained:

$$C_{\mathrm{BC,max}} = \frac{t_s M_B}{t_w V_W} \tag{25}$$

where V_W (= 0.018 m^3/kmol) is the molar volume of pure water and M_B is the molecular mass of the generic solute. The effective t_W value depends on the electromembrane used and was found to vary in the range 2–10 in the case of water desalination (Lee *et al.*, 2002a) and 14–26 in the case of sodium acetate or lactate recovery (Boniardi *et al.*, 1996; Chukwu and Cheryan, 1999; Fidaleo and Moresi, 2004, 2005b; Yen and Cheryan, 1993). Thus, such a large variation in t_W results in quite different $C_{\mathrm{BC,max}}$ values.

F. FOULING AND SCALING OF ELECTROMEMBRANES

Membrane fouling or scaling is generally due to the organic or inorganic substances that are present in the solution to be electrodialytically treated. These may deposit onto the membrane surface or inside the membrane, thus resulting in a decline in the solute permeation flux and an increase in the electrical resistance and energy consumption of the ED stack. To restore the original membrane performance, membrane cleaning is carried out from time to time. Whether the fouling is irreversible, membranes are to be replaced. Both cases affect the ED process economics, membrane cleaning and replacement accounting up to 47% of the overall water desalting costs (Grebenyuk *et al.*, 1998).

When internal fouling takes place, the transport of ions through the electromembrane is hindered by slow-moving organic molecules in the membrane and/or by adsorption or precipitation of organic molecules in the membrane restricting the free-flow area of the membrane. External fouling occurs when a layer of precipitated or adsorbed organic molecules on the membrane surface adds an additional transport resistance to the intrinsic resistance of the membrane.

The precipitation mechanism is governed by the solubility of the foulant, while the adsorption is affected by electrostatic and hydrophobic interactions between the foulant and the membrane surface. The molecular size and the pH of the solution affect the solubility of organic acids. The larger the molecules the lower their solubility and mobility in the membrane become, this improving their adsorption affinity to the membrane. Consequently, fouling cannot be predicted simply by measuring the concentration of the organic matter present in the feed (Lindstrand *et al.*, 2000). First of all, the foulants are to be identified and their solubility has to be taken into account when predicting the degree of fouling.

Numerous foulants are known. It is worth citing some anionic surfactants such as sodium octanoate and sodium dodecylbenzene sulfonate (Lindstrand *et al.*, 2000), sulfonated lignin (Watkins and Pfromm, 1999), sodium humate (Korngold *et al.*, 1970; Lee *et al.*, 2002a), starch, gelatin, egg albumin (De Korosy *et al.*, 1970), grape must (Audinos, 1989), and milk whey (Lonergan *et al.*, 1982).

Table V classifies the main types of foulants together with their charge and methods used to prevent their fouling aptitude.

Among the numerous approaches studied so far to minimize such phenomena in ED, it is worth citing pretreatment of the feed solution by coagulation (De Korosy *et al.*, 1970) or microfiltration (MF) or ultrafiltration membrane processing (Ferrarini, 2001; Lewandowski *et al.*, 1999; Pinacci *et al.*, 2004), turbulence in the compartments, optimization of the process conditions, as well as modification of the membrane properties (Grebenyuk *et al.*, 1998). However, all these methods are partially effective and hydraulic or chemical cleaning-in-place (CIP) is still needed today, thus

TABLE V

MAIN FOULANT CATEGORIES, TYPES, AND CHARGE, AS WELL AS ANTIFOULING METHODS[a]

Foulant category	Type	Electric charge	Tendency to	Fouling prevention method
Scale	$CaCO_3$, $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$, etc.	Neutral	Precipitate on membrane surface	pH adjustment, EDTA or CA addition; lower concentration ratio
Colloids	SiO_2, $Fe(OH)_3$, $Al(OH)_3$, etc.	Negative	Agglomerate on membrane surface	MF or UF feed pretreatment; higher feed flow rate; lower concentration ratio
Organics	Polysaccharides, proteins, polyelectrolytes, humate, surfactans, etc.	Negative	Attach to membrane surface	AC, MF, or UF feed pretreatment; alkali rinsing, EDR process

[a] As extracted from Lee *et al.* (2002b).

AC, activated carbon; CA, citric acid; EDR, electrodialysis reversal; EDTA, ethylenediaminetetraacetic acid; MF, microfiltration; UF, ultrafiltration.

asking for additional chemicals or instruments that expand the investment and operating costs.

Many fouling indices have been defined to describe quantitatively fouling phenomena, such as the silt density index (SDI) and the modified fouling index (MFI) in membrane processing (Schippers and Verdouw, 1980). Actually, MFI was intended to be an aid in predicting the rate of fouling of reverse osmosis (RO) membranes by a specific type of water. It can be easily determined by plotting the ratio between the filtration time and filtrate volume as a function of total filtrate volume. In this way, three different regions can be generally identified in which blocking filtration, cake or gel filtration without or with compression consecutively occur. The linear section of the curve shows the contribution of the cake or gel filtration without compression and its slope represents the MFI, which is a measure of the fouling tendency of the feed under study (Schippers and Verdouw, 1980).

Such an index may be useful in the case of uncharged foulants, but it should be insufficient to assess the rate of fouling in ED membranes. To this end, another fouling index for ED was proposed by Lee *et al.*, 2002b. In presence of an electric field as that shown in Figure 9, the negatively charged foulants tend to migrate toward the anion-exchange membranes. Being rejected by the perm-selectivity of the anionic membranes, these foulants accumulate on the membrane surface owing to the concentration polarization phenomenon. As the foulant concentration at the membrane surface exceeds its saturation or gel concentration, the foulant precipitates, thus forming a fouling gel layer attached to the membrane surface. As the operation proceeds, such a layer becomes thicker and more compact, thus hindering the anions migration across the anionic membranes. Moreover, in accordance with the second Ohm's law the electrical resistance of the fouling gel layer (R_{fg}) will progressively augment as its thickness (δ_{gel}) increases, thus asking for a greater overall potential drop (E) across the ED stack of concern to keep the electric current constant through the process. Both the gel concentration (c_{gel}) and electric conductivity (χ_{gel}) vary with the size, shape, and chemical structure of the foulant, as well as the hydrophilicity of the membranes (Lee *et al.*, 2002b). Thus, the overall electric resistance (R) of the ED stack, as expressed by Eq. 19, has to include the additional term R_{fg}, which is proportional to the electrical charge Q ($= I\,\theta$) passed through the ED stack (Lee *et al.*, 2002b). In the circumstances Eq. 18 can be expressed as

$$E - E_{\mathrm{el}} + (E_{\mathrm{j}} + E_{\mathrm{D}})N_{\mathrm{cell}} = (R + R_{\mathrm{fg}})I \tag{26}$$

Under the constant electric current operating condition, all the terms in Eq. 26 except R_{fg} are independent of time for the continuous mode, this being also approximately valid at the beginning of ED processes operating in the batch mode. Thus, by dividing both members of Eq. 26 by the square of I, the following can be obtained:

$$\frac{E(\theta)}{I^2} \approx \text{const} + \Psi_{\text{ED}}\theta \tag{27}$$

where Ψ_{ED} is the slope of the plot of the $E(\theta)/I^2$ *versus* time (θ), this being defined as the *ED membrane-fouling index* by Lee *et al.* (2002b). The greater such an index the greater the fouling potential for the foulant under testing will be.

Grebenyuk *et al.* (1998) suggested another method to assess the membrane stability against fouling. It was based on the ratio between the overall energy consumption (L) and Coulomb's efficiency (Ω_C) during a real ED process to that observed in ideally nonfouled (K_f) or modified (K_s) membranes.

Watkins and Pfromm (1999) suggested a further method based on capacitance spectroscopy in the range 10^2–10^5 Hz to identify and tracking membrane fouling with organic macromolecules, such as sulfonated lignin, in real times.

Lindstrand *et al.* (2000) investigated the effect of different organic foulants, such as octanoic acid, sodium octonate, and sodium dodecylbenzene sulfonate, on anionic and cationic membranes by monitoring the increase in the membrane resistance (R_m) with time.

Finally, use of square (Lee *et al.*, 2002b) or half (Lee *et al.*, 2003) wave-pulsed electric fields of given frequency was found to be effective to mitigate anionic membrane fouling in presence of sodium humate.

By using a few surfactants, such as oligourethanes with three polar groups (i.e., the so-called trianchor compounds, A-3) or the disodium salt (NB-8) of the α,ω-oligooxipropylene-bis(o-urethane-2.4,2.6-tolueneurylbenzensulphonic acid), at different concentrations, it was possible to minimize membrane fouling in virtue of the formation of a surface protective layer with a charge opposite to that of the base membrane, which was capable of rejecting antipolar ions. However, such modifying substances are to be harmless and safely linked to the membrane surface to avoid any leaching in the food solution undergoing treatment. Moreover, the capability of such layers to generate H^+ and OH^- ions is to be accounted for. For instance, the competing transfer of such ions may reduce the current efficiency (Ω_C), while an increase in the alkalinity of the concentrating stream may lead to the formation of lowly soluble hydroxides, as well as calcium and/or magnesium carbonates, which deposit on the membrane surface (Grebenyuk *et al.*, 1998). Such a deposit was also detected on the cationic membrane side in contact with the alkaline solution during skim milk electro-acidification (Bazinet *et al.*, 2000a).

In conclusion, the anionic membranes appear to be more prone to be fouled by organic matter (De Korosy *et al.*, 1970; Grebenyuk *et al.*, 1998; Lee *et al.*, 2002a, 2003; Lindstrand *et al.*, 2000), while the cationic ones to be scaled by inorganic matter (Atamanenko *et al.*, 2004; Bazinet *et al.*, 2000; Lindstrand *et al.*, 2000). Thus, it is actually impossible to recommend any general procedure to moderate fouling and scaling in ED processing and there is a need for additional research on this issue so that the process can be optimized taking scaling and fouling into account.

III. ED APPLICATIONS

The present ED industry has experienced a steady growth rate of about 15% since 15 years (Srikanth, 2004). The most important industrial ED application is still the production of potable water from brackish water. However, other applications either in the semiconductor industry for the production of ultrapure, that is, completely deionized water without the chemical regenerations of IERs or in the food industry (i.e., whey demineralization, tartaric stabilization of wine, fruit juice deacidification, and molasses desalting) are gaining increasing importance with large-scale industrial installations.

Table VI shows a synopsis of the main industrial ED applications in the food sector.

A few selected examples will be briefly pointed out in the following sections.

TABLE VI

MAIN APPLICATIONS OF THE ED IN THE FOOD SECTOR

Application	Example
Fractionation	Brackish water desalination
	Nitrate removal from drinking water
	NaCl removal from amino acid solutions
	Cheese whey demineralization
	Desalting of protein hydrolysates (i.e., soy sauce), sugar solutions, molasses, and polysaccharide dispersions
	Deacidification of fruit juices
	Tartaric wine stabilization
	Flavor recover from pickle brines
Concentration	Edible table salt production from seawater
	Salts of organic acids from exhausted fermentation media
	Amino acids from protein hydrolysates
Splitting	Conversion of salts into their corresponding free acids and bases

A. BRACKISH AND SEAWATER DESALINATION

Depending on the total dissolved solid content (TDS, expressed in ppm or g/m^3), water may be classified as (http://www.tcn.zaq.ne.jp/membrane/english/DesalE.htm):

- Fresh Water: <1000 TDS
- Brackish: 1000–5000 TDS
- Highly Brackish: 5000–15,000 TDS
- Saline: 15,000–30,000 TDS
- Sea Water: 30,000–40,000 TDS
- Brine: 40,000–300,000 TDS

A variety of desalting technologies has been developed over the last 40 years. Based on their commercial success, they can be classified into major (viz., multistage flash distillation, MSFD; multiple-effect distillation, MED; vapor compression, VC; ED; RO) and minor (i.e., freezing, membrane distillation; solar humidification) processes.

In the inventory compiled for the International Desalination Association (IDA) by Wangnick (1998) the total capacity of installed desalination plants worldwide was estimated as equal to 22.7×10^6 m^3/day, almost half of which was used in the Middle East and North Africa (http://www.membranes-amta.org/media/pdf/reliable.pdf). About 24% of the world's capacity was concentrated in Saudi Arabia, most of which derived from distillation processes. About 16% was produced in the United States by resorting to RO-treated brackish water. MSFD and RO processes made up to about 86% of the total capacity, while the remaining 14% consisted of MED, ED, and VC processes, all the minor processes amounting to less than 1%. Despite the larger number of RO plants, MSFD plants have a higher total production capacity than any other process.

Table VII lists the global production of desalinated water, by process and plant capacity, as extracted from Wangnick (1998) and web site (http://www.desware.net/desa3.aspx).

Figure 11 shows a simplified schematic of a modern ED brackish water desalination plant. Similar to RO, ED plants require water pretreatment to maximize their performance. Coarse and 5- to 10-μm cartridge filtration prevents large particles from plugging the narrow channels of ED stacks. If the raw water Fe^{2+} or Mn^{2+} ion content is greater than 0.3 or 0.1 g/m^3, respectively, an oxidation step followed by filtration is needed to remove the insoluble Fe^{3+} or Mn^{4+} species formed. Raw water must also be accurately filtered to reduce turbidity and colloidal substances (silica), thus minimizing fouling. Chlorination is generally used to control biological fouling (as due to microorganisms, algae, and so on). Dechlorination via activated carbon

TABLE VII

SUMMARY OF WORLDWIDE DESALINATION CAPACITY TILL 1998, SPLIT BY PLANT TYPE AND PROCESS CAPACITY IN THE RANGE 100–60,000 m^3/day[a]

Desalting process	Percentage (%)	Capacity ($\times 10^{-6}$ m^3/day)	No. of plants
Multistage flash	44.4	10.02	1244
Reverse osmosis	39.1	8.83	7851
Multiple effect	4.1	0.92	682
Electrodialysis	5.6	1.27	1470
Vapor compression	4.3	0.97	903
Membrane softening	2.0	0.45	101
Hybrid	0.2	0.05	62
Others	0.3	0.06	120
Overall	100.0	22.57	12,433

[a] Wangnick (1998).

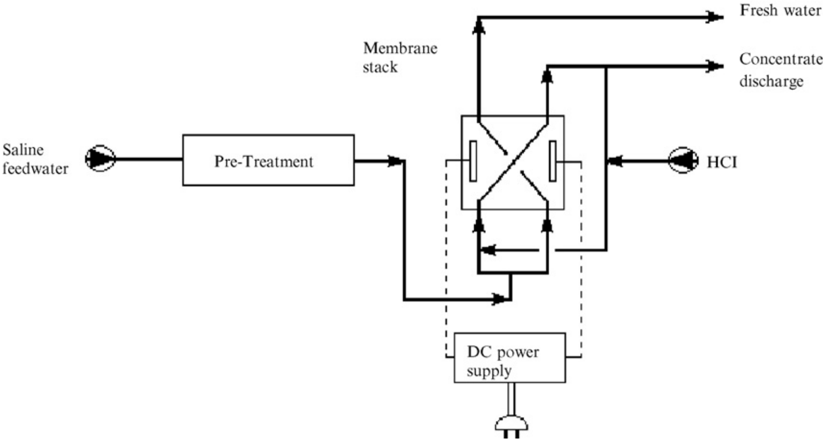


FIG. 11 Simplified schematic of a modern ED brackish water desalination plant.

filters or sodium bisulphite addition is required before water is fed into RO or ED modules, since both membranes are respectively more or less damaged by dissolved free chlorine. Well water with H_2S content greater than 0.3 g/m^3 is to be aerated and/or chlorinated to avoid fouling from elementary sulfur that results from H_2S oxidation in water. Scaling in the concentrating compartments by $CaCO_3$, $CaSO_4$, $BaSO_4$, and $SrSO_4$ decreases stack efficiency and is circumvented by adding an acid (i.e., HCl) or an inhibitor (i.e., sodium hexametaphosphate) into the brine stream or by using the EDR process. The latter is largely more complex than the ED conventional system owing to the automatic valves in the external piping that reverse the feed stream to the brine compartment and the product stream to the diluting one. Moreover, periodic acid cleaning is still required. By reversing the electrode polarity no more than four times per hour and using a 2-minute purge, it is possible to limit production losses to less than 13%.

In the case of a feed TDS ranging from 1.5 to 2 kg/m^3, the energy consumption is of the order of 1.6–2.6 kWh/m^3 of treated water. In the circumstances, there is no need to remove organic matter, colloids, and SiO_2 from raw water, while treated water is just chlorinated for disinfection. On the contrary, degasification and alkaline injection for pH adjustment are used with RO systems. Also, caustic neutralization is needed before RO retentate is discharged to the environment.

The main bottlenecks of RO processes are thus water pretreatment and post-treatment owing to higher RO membrane sensitivity to different organic and inorganic impurities, smaller water recovery (65–75% vs 80–90%), and shorter membrane lifespan (5–7 years against 7–10 years) with respect to ED membranes (Pilat, 2001). With water salinity up to 5000 ppm, ED is generally regarded as the most economic desalination process, while at TDS values higher than 12 kg/m^3 RO is more profitable than conventional ED units as far as power consumption is accounted for (Pilat, 2001). However, the overall energy consumed to desalt seawater using a cascade of two electrodialyzers, equipped with Asahi Glass CMV and AMV membranes (Table II) at current densities of 300–600 A/m^2 in the 1st stage and 300 A/m^2 in the second one, was estimated as equal to 6.6–8.7 kWh/m^3 of treated water at TDS of 0.45 kg/m^3, thus involving a desalination cost of US$1.05 per m^3 (Turek, 2003a).

Today, drinking water supply systems are still lacking in many countries of Asia, Africa, and South America and this makes the market of seawater desalination extremely larger than that of brackish water one. To this end, quite useful portable ED units are currently manufactured by EIKOS Co. (Almaty, Kazakhstan; http://www.eikos.ru/pageng/Eindex.htm), that can be simply connected to the kitchen tap through a flexible tube and, once switched on, can provide individual houses, hospitals, restaurants, and cottages with 5–130 dm^3/h of potable water (Pilat, 2001).

There is also interest in water desalination by solar-powered ED processes (AlMadani, 2003), especially in many Arabic countries where solar energy is available from 10 to 13 hours of sunshine per day during winter- and summertime, respectively. By using a small-scale commercial ED stack, equipped with 24 cell pairs, arranged in four hydraulic stages, and powered by photovoltaic cells, it was possible to desalt laboratory or groundwater of medium salinity at different degrees by varying the operating temperature and product flow rate in the ranges 10–40°C and 8–47 dm^3/h, respectively.

ED is also applied to remove nitrates in drinking water. Owing to the intensive utilization of fertilizers in EU and US agriculture over the last decades, the concentration of nitrates in surface and underground water has steadily increased up to exceed largely the maximum EU (and WHO) norm of 50 g/m^3 for use as drinking water. Among the available competitive techniques (biological processes, BP; IER; and RO) for nitrate removal, the EDR system has the main advantages of high selectivity and water recovery yields of 96–98%, while it suffers from the same disadvantage of IER and RO of asking for further treatment to dispose the concentrate off. On the contrary, BPs allow nitrates to be directly degraded to molecular nitrogen, even if such a process is lengthy and needs bioreactors of quite large volumes.

Several EDR plants with capacity ranging from 120 to 3500 m^3/day have been operating since the early 1990s in the EU. Use of monovalent-selective anion-exchange membranes allowed a selective removal of nitrates over other anions such as chlorides, bicarbonates, and sulfates. Table VIII shows the average composition, pH, and electric conductivity of raw and treated waters, as resulted from about 5-week continuous operation in an EDR pilot unit installed in Vouillé (France) (http://www.ameridia.com/html/ele.html). The raw water was filtrated using a 10-μm cartridge filter and fed to the pilot unit by the well pump at 13°C and a flow rate of 11.5 m^3/h. Automatic polarity and hydraulic inversion was carried out three times per hour to avoid any eventual membrane fouling. Moreover, about 0.6 m^3/h of feed water was used to dilute the concentrated loop. In this way, it was possible to achieve a 69% nitrate removal yield with a 95% water recovery and a power consumption of approximately 0.1 kWh/m^3 of treated water.

TABLE VIII

AVERAGE PERFORMANCE OF A 50-m^2 EDR PILOT UNIT INSTALLED IN VOUILLÉ (FRANCE) THROUGHOUT A 5-WEEK CONTINUOUS OPERATION TO DESALT DRINKING WATER[a]

Parameter	Unit	Raw water	Treated water	Removal efficiency (%)
Ca^{2+}	g/m^3	108	61	44
Mg^{2+}	g/m^3	3	2	35
Na^+	g/m^3	13	12	8
K^+	g/m^3	1	1	0
HCO_3^-	g/m^3	250	171	32
Cl^-	g/m^3	25	12	52
SO_4^{2-}	g/m^3	18	17	6
NO_3^-	g/m^3	75	23	69
pH	–	7.9	7.7	3
Total dissolved solids	g/m^3	492	298	39
Electric conductivity	S/m	55.4	34.3	40

[a] http://www.ameridia.com/html/ele.html

The waste stream from any desalination process contains the salts removed from the saline feed to produce the fresh water product, as well as some of the chemicals added and corrosion by-products. Thus, its disposal may cause environmental problems. If the desalting plant is located near the sea, its disposal in the sea may be a minor problem provided that environmental changes related to the receiving waters for the accumulation of added constituents, dissolved oxygen levels, and different water temperatures are taken into account. If the desalting plant is sited inland, away from a natural saltwater body, waste disposal may involve dilution, injection into a saline aquifer, evaporation, or transport by pipeline to a suitable disposal point. Thus, the overall operating costs for a desalination plant depend on its capacity, type, and location, feed water, labor, energy, financing, concentrate disposal, and plant reliability. In general, the cost of desalted seawater is about three to five times greater than that of desalted brackish water when using the same plant size.

B. TABLE SALT PRODUCTION

The production of table salt from seawater, by the use of ED to concentrate sodium chloride up to 200 kg/m^3 prior to evaporation and salt crystallization, has achieved a certain commercial importance, especially in Japan and Kuwait, even if it seems to be highly subsidized (Strathmann, 1992). The key to the success of this technology has been the low-cost, highly conductive membranes with a preferred permeability of monovalent ions. This allowed chloride ions to be cumulated in the concentrated stream, while Ca^{2+} and Mg^{2+} ions and sulfates were quite totally rejected in the diluting stream.

More recently, Turek (2003b) suggested to desalt further such a diluate to produce potable water and reduce the overall ED-operating costs. Owing to the difficulty of such an operation, being the salinity of partially desalinated water as high as 22.9 kg/m^3 of TDS, such a stream was treated by using another EDR stage equipped with normal grade CMV, AMV Asahi Glass membranes (Table II), thus avoiding gypsum crystallization in the concentrated stream and yielding 90% recovery. By assuming the salt sell price at US$30 per metric ton (Mg), the potable water cost was estimated as US$0.44 per m^3.

C. DAIRY INDUSTRY

In the dairy industry the high content of minerals in cow milk (Table IX) restricts the commercial utilization of its main by-products, that is, whey and ultrafiltration permeates. The discovery that desalted whey could be used in baby food production as an economic alternative to the more expensive skim

TABLE IX

AVERAGE pH, BIOLOGICAL OXYGEN DEMAND (BOD_5), AND GROSS COMPOSITION OF COW MILK AND SWEET OR ACID WHEY[a]

Component	Cow milk	Sweet whey	Acid whey	Unit
pH	6.9	<6	<4	–
BOD_5	–	31	35	kg/m^3
Water	87.13	93.6	93.5	% w/w
Dry matter	12.87	6.4	6.5	% w/w
Lactose	4.9	4.9–5.0	4.48–4.76	% w/w
Lactic acid	–	0.03–0.04	0.42–0.49	% w/w
Raw protein	3.37	0.84–1.10	0.84–1.10	% w/w
Fat	3.9	0.06–0.07	0.03–0.04	% w/w
Ash	0.7	0.49–0.56	0.67–0.81	% w/w

[a] Moresi (1981), Zall (1992).

milk converted whey, a troublesome effluent to dispose of, into a value-added raw product. Thus, whey de-ashing has become a prerequisite to produce infant formulae closely resembling human milk, as well as to lactose crystallization or hydrolysis (Hoppe and Higgins, 1992).

Whey is a yellow–green liquid which is the major by-product of cheese making, the weight ratio of whey to cheese ranging from 9 to 11. It easily acidifies and can be distinguished into sweet or acid whey. Table IX shows its average composition (expressed as weight fraction), pH, and biological oxygen demand (BOD_5). It contains 4.5–5.0% lactose, 0.04% nitrogen components and approximately 0.5% ash. Its economical use is influenced by the high water content (94–95%). Owing to its BOD_5 content varying from 30 to 45 kg/m^3, whey cannot be directly discharged as wastewater into sewage.

The first commercial whey-processing ED plant was commissioned in 1961 (Stribley, 1963), while the first European plant was bespoke in Holland in 1963 (Batchelder, 1987). They consisted of a typical monopolar two-compartment ED process equipped with tortuous-path or sheet-flow spacer gaskets (Figure 6) and operated in the batch or continuous mode (Figure 7) provided that a 90–95% or 60–75% decrease in ash is to be respectively achieved (Ahlgren, 1972; Batchelder, 1987). According to Iaconelli (1973), the output capacity of an ED plant doubles or quadruplicates if the demineralization degree is reduced from 90% to 75% or 50%, respectively. Also the electric power consumption depends on the de-ashing level being not greater than 1 kWh/kg of ash removed if the demineralization degree is ranging from 50% to 75% (Ahlgren, 1972).

The ion removal medium is generally a sodium chloride solution, while the ideal electrode-rinsing solution contains sodium sulfate rather than sodium chloride to avoid chlorine evolution at the anode compartment (Shaffer and Mintz, 1966). Lifelong stainless steel or graphite electrodes are generally used, these being designed to operate also in the current reversal mode (EDR) (http://www.ameridia.com/html/dry.html).

The optimal performance of whey de-ashing is determined by many factors depending on feedstock composition and de-ashing degree.

By increasing whey concentration up to 15–20% TDS (w/v), the increase in electric conductivity enhances the Faraday efficiency with no counter effect resulting from the concomitant increase in solution viscosity (de Boer and Robbertsen, 1983; Johnson *et al.*, 1976). The optimal temperature is a compromise between de-ashing rates, which increase in the range of 30–40°C, and bacteriological control, which is ideal at about 10°C (de Boer and Robbertsen, 1983). Any increase in temperature beyond 40°C was found to be ineffective because of protein agglomeration. This gives rise to particulate deposition onto the membrane surfaces, thus enhancing the polarization layer and overall stack resistance, and finally can lead to channel blocking and eventually to electrical short circuit.

During whey de-ashing by ED, multivalent ions (viz., PO_4^{-3} e Ca^{+2}) are generally removed after the monovalent ones (i.e., Cl^-, K^+, Na^+) have been essentially removed (Ahlgren, 1972; de Boer and Robbertsen, 1983; Hoppe and Higgins, 1992). For instance, conventional ED of an ultrafiltered (UF) permeate of *Grana* cheese whey allowed the ash content to be reduced from 0.42% to 0.05% (w/w), thus involving practically 100% reduction in the Na^+, K^+, and Cl^- ion contents, about 90% decrease in PO_4^{3-} anion level, and just as little as 25% decline in Ca^{2+} and Mg^{2+} cation concentrations (Mucchetti and Taglietti, 1993). To enhance removal of the latter, whey may be decalcified by using weak-acid IER in the sodium form (de Boer and Robbertsen, 1983) or acidified to a pH of about 4.6 (D'Souza *et al.*, 1973; de Boer and Robbertsen, 1983). Such a pH value, being quite coincident with the protein isoelectric point, was found to be optimal both for calcium solubility and for the removal rate of calcium salts, cation and anion transport being unhindered by charged protein groups (D'Souza *et al.*, 1973; de Boer and Robbertsen, 1983).

Demineralization of UF whey retentate as compared to UF whey permeate is generally slowed down by salt and/or proteins that build up onto and in the membranes (Pérez *et al.*, 1994). Finally, in the case of skim milk the aim of the ED process is not only to reduce the overall ash content, but also to increase the calcium/phosphate ratio to about 0.77 in skim milk powder used in infant formula (Batchelder, 1987), this goal being much easily achievable by replacing the conventional membranes with selective ones (Andrés *et al.*, 1995).

Membrane scaling and fouling are critical points in whey demineralization by ED. Whereas scaling is due to precipitation of $CaCO_3$, $CaSO_4$, $Ca_3(PO_3)_2$ on the brine side of the cationic membranes and can be easily removed by a normal acid cleaning, organic fouling is due to precipitation of charged protein fractions, as well as amino acids, onto the surfaces or pores of the anionic membranes, but it is poorly removed by normal CIP techniques, thus causing the continuous increase in the stack overall resistance and decline in process performance.

To minimize membrane fouling it was suggested to replace the anionic membranes with neutral cellulose-based membranes, such as the dialysis membranes (Ahlgren, 1972), thus leading to the so-called *transport-depletion ED* (TDED) process, as schematically shown in Figure 12. In this way, the only anion transport is limited, whereas cations can pass through any membrane and cumulate into the concentrating compartments. Even if the current efficiency of the process is approximately halved, the savings in membrane investment and replacement costs, as well as in CIP procedures, resulted in overall processing costs of the same order of magnitude of those associated to conventional ED, where the current efficiency initially approaching 100% progressively reduces to less than 50% owing to protein

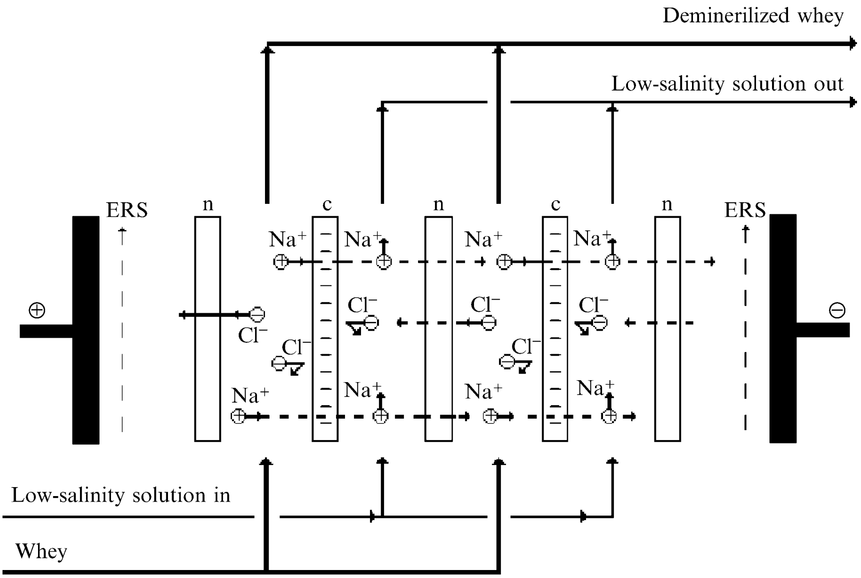


FIG. 12 Schematic layout of a transport depletion ED stack used to demineralize whey: c, cationic membrane; ERS, electrode-rinsing solution; n, neutral membrane.

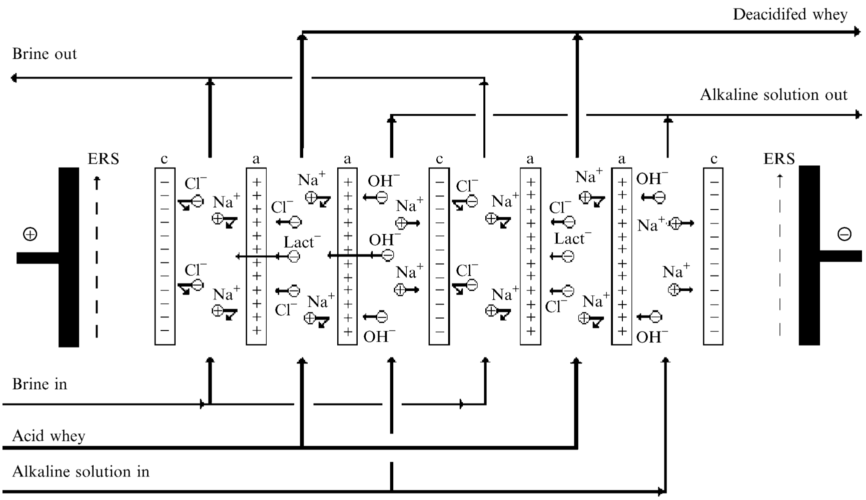


FIG. 13 Schematic layout of a three-compartment ED stack used to desalt acid whey: a, anionic membrane; c, cationic membrane; ERS, electrode-rinsing solution.

deposition onto and within anionic membranes (Ahlgren, 1972). Nevertheless, TDED process seems to have been overcome by the EDR process, which is today the process of choice in whey demineralization (http://www.ameridia.com; http://www.ionics.com).

When dealing with acid whey, and lactate removal is a priority task, it is possible to resort to a three-compartment configuration (Figure 13), obtained by assembling a series of two anionic membranes and a single cationic one (Williams and Kline, 1980). By feeding the compartments limited by two anionic membranes with acid whey and the other two adjacent compartments with a brine solution and an alkaline one, respectively, it is possible to remove selectively lactate anions from the product and replace them with hydroxyl ions. This procedure is also suggested to reduce the acidity of several acidic fruit juices without any chemical addition (Section III.E).

Besides ED, a number of other commercial processes using ion exchange (IE) or nanofiltration (NF) has been proposed for whey demineralization (Greiter *et al.*, 2004; Hoppe and Higgins, 1992). However, it is still impossible to assess definitively which is the optimal process for whey de-ashing, its capital and operating costs depending on several financial, operational, and geographical factors.

As an example, by referring to an IE or ED de-ashing unit with an overall capacity of 45 m^3/day of nanofiltrated whey (three times concentrated and partially desalted), Greiter *et al.* (2002) estimated that the cumulative energy

TABLE X

WHEY DEMINERALIZATION USING AN IE OR ED UNIT WITH AN OVERALL CAPACITY OF 45 m^3/DAY OF NANOFILTRATED WHEY: COMPARISON OF WASTEWATER FORMATION AND ENERGY DEMAND[a]

Alternative technology			
Parameter	IE	ED	Unit
Demineralization level	99	90	%
Wastewater formation			
Volume	3.7	1.25	m^3
Ash content	36.3	8.1	kg
Organic load (COD)	26.0	8.4	kg/m^3
Energy demand for			
Pumping	0.15	4.2	kWh/m^3
Production of regenerants	25.3	–	kWh/m^3
Electrodialysis desalting	–	5.4	kWh/m^3
Reduction of the organic load	9.8	3.2	kWh/m^3

[a] Greiter *et al.* (2002).

Note: IE, ion exchange; ED, electrodialysis.

demand for pumping, producing the IE regenerants, and reducing the organic charge of wastewaters in the case of the IE unit was about three times greater than that in the ED one (Table X). Even if their corresponding overall de-ashing rates were set to 99% or 90%, respectively, the volume, ash content, and organic load of IE effluents were from three to four times greater than those of ED ones (Table X). Despite this clearly proved the greater sustainability of ED with respect to IE, additional aspects, such as regenerant transportation, energy demand for resin production, membrane specific costs, and so on, as well as IE or ED process improvement, are to be accounted for. To this end, it is worth citing the ammonium bicarbonate or SMR process (*Svenska Mejeriernas Riksforening* or Swedish Dairy Association) as an example of how the use of a single regenerant (NH_4HCO_3) can reduce regenerant consumption by recycling, as well as associated waste disposal problems and costs (Hoppe and Higgins, 1992; Jönsson and Olsson, 1981). See also the comments on different ED processes reported earlier.

Today, improvement and economic evaluation of such competing technologies seem to identify the optimum process for whey demineralization as a hybrid process combining EDR, IE, and NF depending on the target de-ashing level (Table XI) (http://www.ameridia.com/html/dry.html). For instance, a single NF unit is regarded as inappropriate for demineralization rates greater than 35–40% because of high loss of lactose and divalent ions, but useful as a pre- or post-treatment step. This was also verified in the case

TABLE XI

SINGLE OR HYBRID PROCESS, BASED ON ED, IE, AND/OR NF, RECOMMENDED BY EURODIA/AMERIDIA TO DEMINERALIZE RAW OR PRECONCENTRATED WHEY AS A FUNCTION OF DIFFERENT DE-ASHING LEVELS[a]

	Feed total solid content (% w/w)	
De-ashing level (%)	6	18–24
30	NF	ED
50–70	IE + NF	ED
90	ED + IE + NF	IE + ED

[a] http://www.ameridia.com/html/dry.html

Note: ED, electrodialysis; IE, ion exchange; NF, nanofiltration.

of lactic acid recovery, its average recovery yield being of the order of 61% for ED against 53% for NF. Even a single IE unit is regarded as uneconomical because of high volume of effluents and heavy pollution load (Greiter *et al.*, 2002). These findings are also confirmed in Table XII, where the estimated specific overall costs to manufacture 90%-de-ashed whey powder are compared by referring to an industrial plant with a daily capacity of 400 m^3 of raw whey at 6.3% TDS using a single or hybrid process (http://www.ameridia.com/html/dry.html).

To separate the major protein constituents of whey, such as β-lactoglobulin (β-LG) and α-lactoalbumin (α-LA), Bazinet *et al.* (2004) recommended the use of bipolar membrane electroacidification (BMEA) by resorting to a three-compartment ED stack consisting of a bipolar membrane and two cationic membranes in parallel. Recycling of 5–20% (w/w) whey protein isolate (WPI) solutions in the compartments edging the cationic side of any bipolar membrane, where the H$^+$ ions are generated, allowed the pH to be lowered from about 6.9 to 4.6. Further centrifugation of the resulting acidic solution enabled about 53% of the initial β-LG to be recovered, thus yielding a residue, containing about 97% of β-LG and 2.7% of α-LA, and an α-LA-enriched supernatant (Bazinet *et al.*, 2004). This procedure proved not only much simpler, but also more effective than the numerous isolation methods available in the literature and based on ion-exchange chromatography, metaphosphate complex precipitation, heat/acid separation, and ion depletion at low pH. For instance, the procedure developed by Slack *et al.* (1986) yielded β-LG-enriched fractions containing just 33% of the original acid whey proteins or 17% of the original sweet whey proteins by submitting whey to concentration by UF; partial demineralization by ED or diafiltration, upon adjustment of the initial and final pH values to 4.65; and finally to centrifugation.

TABLE XII

EFFECT OF A SINGLE OR HYBRID PROCESS, BASED ON ED, IE, AND/OR NF, ON THE OVERALL OPERATING COSTS PER kg OF DM OF 90%-DEMINERALIZED WHEY POWDER, AS ESTIMATED BY EURODIA/AMERIDIA[a] BY REFERRING TO AN INDUSTRIAL PLANT WITH AN INPUT CAPACITY OF 400 m^3/day OF RAW WHEY AT 6.3% TDS[a]

Hybrid process	Demineralization operating costs (€/kg DM)
IE	0.37
IE + ED	0.18
IE + ED + IE	0.06
NF + ED + IE + NF	0.05

[a] http://www.ameridia.com/html/dry.html

Note: ED, electrodialysis; IE, ion exchange; NF, nanofiltration; DM, dry matter.

The BMEA procedure was also used to produce high-purity bovine milk casein (Bazinet *et al.*, 1999a) and soybean isolates (Bazinet *et al.*, 1997; 1999b) or to fractionate soybean 11S and 7S fractions (Bazinet *et al.*, 2000b).

Further information on such a novel process, as well as the preparation of acid caseinates, electrochemical coagulation of milk proteins or electroreduction of disulfide bonds of milk proteins, using conventional or bipolar ED stacks, is given by Bazinet (2004). It is however worthy underlining that all these processes do not seem to have been used on an industrial scale yet.

D. WINE INDUSTRY

One of the main concerns in wine shipping is to avoid tartrate crystal precipitation in bottle. These crystals may be confused with fragments of broken glasses, sugar crystals, or chemical residues, thus inducing wine bottle refusal in the general consumer, especially in the United States and Japan. Moreover, in the case of sparkling wines, such crystals may cause excessive loss of product when the bottle is opened. Hence, there is a great deal of interest to improve wine stability, as well as to resort to reliable stabilization procedures.

Grapes naturally contain quite large levels of tartaric acid (H_2T) and potassium ions of the order of 1–3 and 0.8–1.5 kg/m^3, respectively. Tartaric acid is a weak dicarboxylic one that dissociates into tartrate and bitartrate forms as follows:

$$H_2T \leftrightarrows HT^- + H^+$$

$$HT \leftrightharpoons T^{2-} + H^+$$

It can precipitate as potassium hydrogen tartrate (KHT) or as calcium tartrate (CaT), the latter being practically insoluble in aqueous solutions. Their equilibrium solubility varies with temperature, pH, and alcohol content, while the presence of a few wine components, such as polysaccharides and mannoproteins, may hinder spontaneous nucleation even if the solution is supersaturated. From Figure 14 that shows the equilibrium tartaric acid-dissociated fractions *versus* pH and ethanol volumetric fraction (Berta, 1993; Usseglio-Tomasset and Bosia, 1978), it can be seen that in the typical pH range (3–4) of wines KHT is predominant. As temperature is reduced from 20 to 0°C, KHT solubility in water or in a 12% (v/v) hydro-alcoholic solution reduces from 5.11 to 2.45 kg/m^3 or from 2.75 to 1.1 kg/m^3, respectively (Berta, 1993). Each of these data also varies with pH and reaches a minimum at the pH value associated with the maximum concentration of the hydrogen tartrate anions. For the above-mentioned solutions, the solubility minimum shifts from pH 3.57 to pH 3.73 as the ethanol content increases from 0 to 12% (v/v) (Berta, 1993).

The conventional tartaric stabilization techniques applied in the wine industry are based on two opposite principles. One is aimed at heightening HT^- and T^{2-} precipitation by reducing wine temperature and leads to the so-called cold stabilization technique. To accelerate nucleation, wines are seeded with exogenous KHT crystals, cooled and kept at −4°C for 4–8 days

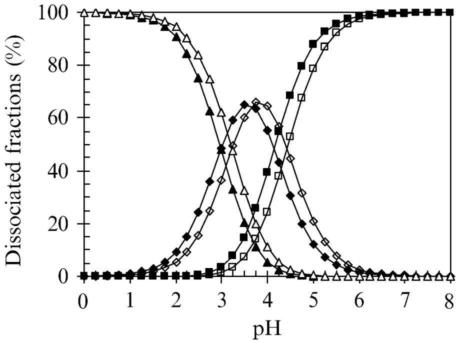


FIG. 14 Effect of pH on the equilibrium tartaric acid dissociated fractions (◆, ◇, [HT^-]/[T]; ■, □, [T^{2-}]/[T]; ▲, △, [H_2T]/[T]) at two different ethanol volumetric fractions (0% v/v, closed symbols; 18% v/v, open symbols), as estimated according to Berta (1993) and Usseglio-Tomasset and Bosia (1978): H_2T, free tartaric acid concentration; HT^-, hydrogen tartrate concentration; T^{2-}, tartrate concentration; T, overall tartaric acid concentration.

to favor crystal growth. The other principle is directed to impair the crystallization process, especially when KHT content is closely exceeding the equilibrium one, by enriching wine with some antiprecipitation additives, such as metatartaric acid, carboxycellulose or yeast mannoproteins.

Despite its quite general application, the refrigeration technique is not only expensive and time-consuming, but also not fully reliable, as KHT crystals can still precipitate during bottle storage and transportation. It may even affect negatively the wine sensory properties as a result of the preliminary wine clarification and crystal removal steps. Thus, the use of IER (Hernàndez and Mínguez, 1997; Mourgues, 1993) and ED has been alternatively proposed to remove K^+ cations. Whereas the former is not allowed in the EU for it alters the ionic balance of wine, as well as its taste, the latter is recognized as a good manufacturing practice by the International Wine Office (OIV) and is approved for commercial use by the EU regulatory no. 2053/97.

Although early ED tests for tartrate stabilization of wines had been performed by Paronetto (1941), more systematic experiments were carried out in the 1970s (Audinos *et al.*, 1979; Paronetto *et al.*, 1977; Wucherpfennig and Krueger, 1975) and led to the automatic method and device for tartaric stabilization of wines developed by Escudier *et al.* (1995) at the French National Agronomic Research Institute (INRA) in cooperation with Ameridia (Moutounet *et al.*, 1997).

Not only does ED allow removal of KHT and tartaric acid in almost the same way observed in the conventional cold-stabilization process, but it also permits a certain degree of reduction in lactic and malic acids, as well as Mg^{2+}, Ca^{2+}, and Na^+ ions, this however being within the limits imposed by the EU regulatory no. 2053/97 (Bach *et al.*, 1999). On the contrary, removal of catechins, leucoanthocyanins, and anthocyanins in ED-stabilized wines was significantly lower than in cold-stabilized ones (Riponi *et al.*, 1992). As an example, Figure 15 shows the percentage removal yields for the main anions and cations present in two typical white and red Portuguese wines as a function of the corresponding percentage reduction in wine electric conductivity (Gonçalves *et al.*, 2003). It can be noted that the removal of calcium is crucial to achieve tartrate stability in terms of both KHT and calcium tartrate.

A number of sensory tests have so far revealed no difference in the organoleptic properties of ED- and cold-stabilized wines (Bach *et al.*, 1999; Cameira dos Santos *et al.*, 2000; Gonçalves *et al.*, 2003; Paronetto *et al.*, 1977; Riponi *et al.*, 1992; Wucherpfennig and Krueger, 1975).

ED treatment may be tailored for any type of wine by referring to a specific stability test. A sample of the raw wine under testing is to be filtered,

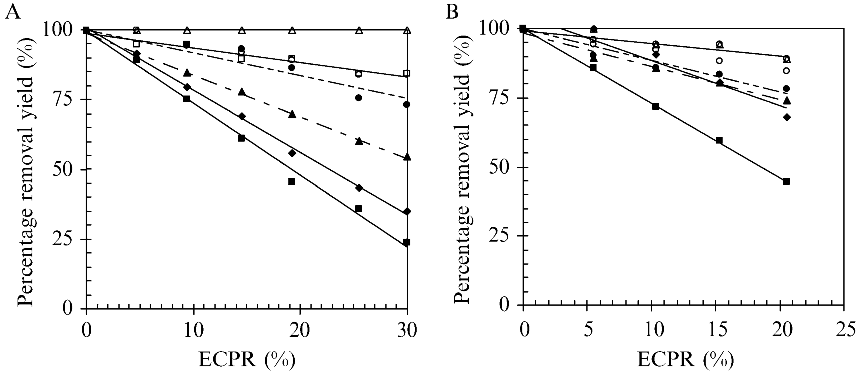


FIG. 15 Percentage removal yields for the main anions (○, tartaric acid; □, malic acid; △, lactic acid) and cations (▲,K^+; ●, Na^+; ■, Ca^{2+}; ◆, Mg^{2+}) present in two typical white (A) and red (B) Portuguese wines as a function of the corresponding percentage reduction in electric conductivity (ECPR), as extracted from Gonçalves *et al.* (2003).

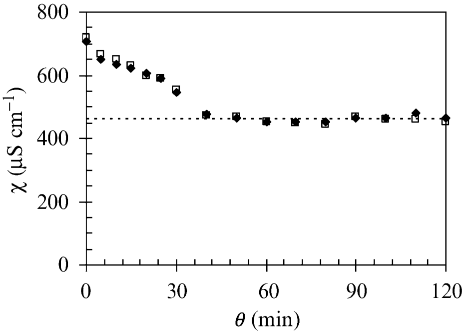


FIG. 16 Stability tests performed on two 200-cm^3 samples, seeded with fine crystals of KHT (4 kg/m^3) and chilled at −4°C, of San Flaviano Est! Est!! Est!!! white wine, manufactured at Montefiascone (Italy) during the 2000 vintage: electric conductivity (χ) vs. time.

seeded with fine crystals of KHT (4 kg/m^3), and then chilled at −4°C, while monitoring the time course of its electric conductivity (χ).

Figure 16 shows the typical evolution of such a test being performed on two 200-cm^3 samples of San Flaviano Est! Est!! Est!!! white wine, manufactured at Montefiascone (Italy) during the 2000 vintage. In less than 1 hour, it was possible to assess the equilibrium χ value (460 ± 9 μS/cm) or how much its initial χ value (721 ± 28 μS/cm) had to be reduced to avoid tartrate precipitation after bottling.

Based on the INRA experience (Escudier *et al.*, 1995), the average drop in χ to stabilize a wine is in the range 5–20% for red wines, but it can exceed 30% for white and young wines.

The ED-treated wines generally result to be completely stable once KHT and CaT have been selectively removed. Their basic characteristics (i.e., pH, acidity, sugar content, alcohol level), as well as taste, bouquet, and color, are practically unaltered, while their ethanol content, pH, and volatile acidity are reduced by less than 0.1% (v/v), 0.25 pH units, and 0.09 kg/m^3 (expressed as equivalent H_2SO_4), respectively (htpp://www.ameridia.com/html/wn.html).

Tartaric stabilization of wines can be performed using a conventional monopolar ED stack operating in the batch mode (Figure 5A). Anionic membranes are more liable to fouling than cationic ones, especially when dealing with red wines, but periodic (once per day) in-site rinsing and cleaning of the ED stack can minimize fouling and extend their life time.

After being microfiltered with no needs of filter aids and/or chemical additives, the raw wine is recirculated between the ED stack and a tank, equipped with level gauges and a conductivity meter. As soon as its conductivity has reached the predetermined equilibrium χ value, it is automatically discharged and replaced with another lot.

The brine solution may be enriched with NaCl or KHT to increase its conductivity and acidified to the same pH of the wine under treatment. It is recirculated between the concentrating compartments of the ED stack and another tank equipped with conductivity and pH automatic controls so as to avoid precipitation of potassium bitartrate onto the membranes by diluting the brine with deionized water and/or discharging more or less aliquots of the brine itself when its conductivity reaches 70–80% of its saturation value (Gonçalves *et al.*, 2003). In this way, a waste effluent in the range 10–20% of the wine volume treated is to be disposed of or used to recover KHT crystals (Nasr-Allah and Audinos, 1994).

For this treatment the typical permeation flux is of the order of 100 dm^{3}m^{-2}h^{-1} of wine treated, while the overall electric energy consumption ranges from 0.5 to 1.0 kWh/m^3, this being about 10 times lower than the energy needed for the refrigeration procedure. For an ED unit treating about 40,000 m^3 of wines per year it was estimated an overall investment of about US$400,000, and operating costs of circa cUS$0.6 per litre of wine treated. For much smaller capacities up to 4500 m^3/year, the ED unit can be installed on a truck and offered on rent at less than cUS$10 per bottle. By the year 2003, Eurodia/Ameridia claimed to have supplied over 40 plants in France, Italy, Spain, Australia, and United States with an overall capacity of 3×10^5 m^3/year (htpp://www.ameridia.com/html/wn.html).

Even in this case, the use of a hybrid process combining NF, IE, and ED appears to improve the economics and performance of the tartaric stabilization of wines. For instance, Ferrarini (2001) proposed to split raw wine into a retentate and permeate by NF. The permeate, being richer in minerals, was processed by using in sequence cationic and anionic exchange resins and ED to reduce its potassium, calcium, and tartrate ion contents. By recombining the de-ashed permeate with the NF retentate, Ferrarini (2001) asserted to obtain a stabilized wine retaining almost all the flavor and aroma compounds originally present in raw wine.

E. FRUIT JUICE INDUSTRY

In this industry ED processing might be applied in three main areas, that is, de-acidification, desalting, and enzymatic-browning inhibition.

Some acidic fruit juices are not fully appreciated by consumers and are to be de-acidified by sugar or alkali addition. Whereas the use of $CaCO_3$ is not recommended since the release of CO_2 induces foaming and poor pH control, that of $Ca(OH)_2$ may cause some precipitation problems in the final product. Such procedures may be limited by legislation and, even if they have so far conferred no sensory dislike, may involve chemophobic reactions in the general consumer, who is averse to any chemical addition in natural products (Vera *et al.*, 2003).

Use of conventional ED stacks composed of alternating cationic and anionic membranes was suggested to reduce the acidity of several fruit juices, such as grape, orange, lemon, pineapple (Adhikary *et al.*, 1983), and *ume* (pickled Japanese apricot) (Ono *et al.*, 1992) juices without any chemical addition. Preliminary clarification of fruit juices via ultrafiltration was found to minimize membrane fouling. In the case of UF mandarin orange juice, ED processing allowed its total acidity to be reduced by 30% with no detectable color change, almost constant ascorbic acid, amino-nitrogen compound, free sugar, and flavonoid contents, and a slight decrease in the pH (Kang and Rhee, 2002). Appropriate UF modules were also used to decolorize date juices before their demineralization via ED and concentration to yield liquid sugar (Lewandowski *et al.*, 1999).

To de-acidify orange juice it was also suggested using an ED stack composed of anionic membranes only and two compartments. In this way, only the anions, mainly citrate, were removed from the juice and replaced by the hydroxyl ions supplied by the KOH solution flowing in the adjacent compartments. Periodic reversal of polarity helped removal of the colloidal material deposited onto the membrane surfaces. Voss (1986) suggested two alternative ED processes. One was a three-compartment stack, obtained by arranging a cationic membrane and two anionic ones in sequence

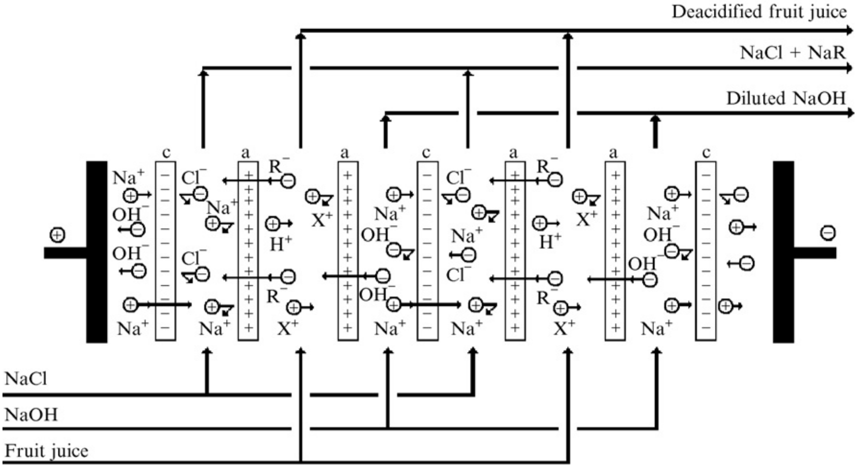


FIG. 17 Schematic layout of a three-compartment ED stack for the deacidification of fruit juices: a, anionic membrane; c, cationic membrane; R^-, generic anion; X^+, generic cation.

(Figure 17), as that used to remove selectively lactic acids from acid whey (Figure 13). The other was a two-compartment stack, made of a bipolar membrane and an anion-exchange one (Figure 8C), to attain a de-acidified juice and a concentrated stream containing free citric acid.

More recently, such processes were tested to reduce the acidity of clarified passion fruit (*Passiflora edulis v. flavicarpa*) juices from pH 2.9 to 4.0 in comparison with other conventional processes, such as calcium citrate precipitation as resulting from $CaCO_3$ or $Ca(OH)_2$ addition, or removal via weakly basic IER (Calle *et al.*, 2002; Vera *et al.*, 2003). Whatever the process tested, the physicochemical and sensory properties of the de-acidified juices were quite similar. In spite of the fact that their sodium concentration was higher when using any of the above-mentioned ED processes, the two-compartment stack using bipolar and anionic membranes (Figure 8C) was regarded as optimal, since no chemical consumption was needed and a valuable solution rich in citric acid (89% purity) was recovered (Vera *et al.*, 2003).

In the production of pickles, salted fruits are generally leached or flushed with water to reduce their sodium content. The waste stream may be split into a sugar-rich solution and a brine via ED. Whereas the latter is recycled to the brining process, the former is reused to return the natural sugar and color to the fruits undergoing leaching (Elankovan, 1996). By coupling ED and adsorption on weakly basic resins, the seasoning solution used to flavor salted ume may be selectively deprived of NaCl and organic acids, thus allowing its remaining sugars and aminoacids to be repeatedly reused (Takatsuji *et al.*, 1999).

Finally, a process was patented to minimize the nitrate nitrogen content in vegetable juices by ED, once concentrated to 20–40°Brix (Sumimura *et al.*, 2004).

There is an increasing consumer demand for cloudy apple juices owing to their greater sensory and nutritional quality. However, such juices are extremely sensitive to taste and color modification for the polyphenol oxidases (PPO) bound to suspended matter catalyze the oxidation of phenolic compounds to o-quinones, which readily polymerize into dark-colored pigments. By acidifying the juice to pH 2.0 (Zemel *et al.*, 1990), it is possible to affect irreversibly the PPO tertiary structure by inducing electrostatic repulsion between acids and positively charged amino groups and thus inhibit PPO activity. To avoid the dilution effect due to subsequent addition of acid (HCl) and base (NaOH), Tronc *et al.* (1998) suggested using ED stacks equipped with bipolar membranes to reduce temporarily the pH of cloudy apple juice to 2.0 and then to readjust its pH to the initial value (3.5). Of the two-compartment configurations, that coupling a bpm with an anion-exchange membrane (Figure 18) was found to be faster and more effective to accelerate the acidification and inhibit enzymic browning. By flowing 0.1 kmol/m^3 HCl between the anionic side of bpms and any anionic membrane, the Cl^- ions can permeate through the anionic membranes and cumulate in the juice, thus promoting the retention of the hydrogen ions generated by the cationic side of bpms. As referring to Figure 18 and reversing the juice and HCl compartments, it was possible to replace the Cl^- ions accumulated in the acidified juice with the hydroxyl ions generated by the anionic side of bpms, thus allowing the pH of the juice to return to its initial value. In this way, it was noted a slight reactivation of PPO activity, but browning inhibition was complete and irreversible. The treatment enhanced the color of cloudy apple juice during storage with a limited effect on its chemical composition and organoleptic quality (Quoc *et al.*, 2000).

F. SUGAR INDUSTRY

Beet or cane molasses are the main by-products in the sugar-manufacturing process. Despite an average sugar content of 50% (w/w), further sugar recovery is hampered by the presence of impurities ranging from suspended materials to inorganic salts and color substances. A great deal of emphasis has been put on the alkali metal cations, namely Na^+, K^+, Ca^{2+}, and Mg^{2+}, these being regarded as melassigenic ions (Elmidaoui *et al.*, 2002, 2004). To get rid of multivalent cations, molasses are generally integrated with lime or

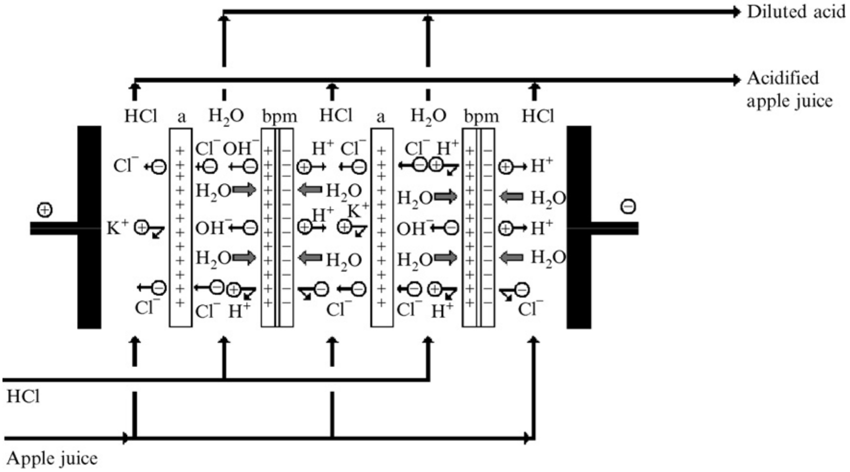


FIG. 18 Schematic layout of a two-compartment configuration using bipolar (bmp) and anionic (a) membranes proposed to inhibit enzymatic browning of cloudy apple juice (Tronc *et al.*, 1998) via preliminary acidification to pH 2.0 and subsequent de-acidification to pH 3.5 by reverting flow of HCl and apple juice streams.

$CaCl_2$ and heated, thus causing precipitation of $CaSO_4$ and $MgSO_4$,, which are then separated by centrifugation. Several alternative processes, such as IER, synthetic adsorbents, coagulants, membrane filtration, and ED, have been proposed so far.

For instance, the sugarcane juice might be clarified via filtration (Thampy *et al.*, 1999) or MF (Pinacci *et al.*, 2004) to minimize fouling phenomena, concentrated to about 30°Brix, desalted by 50–80% using conventional ED, further concentrated, and then crystallized, thus obtaining crystals of uniform size and molasses brown in color, but palatable (Thampy *et al.*, 1999).

The main bottlenecks of ED application in the sugar industry were both the short membrane life, especially for the anion-exchange membranes, and the high viscosity of cane- or beet-sugar syrups, the maximum working temperature for the electromembranes being generally less than 40°C.

By replacing the conventional anionic membranes with the novel ones type Neosepta® AXE 01 (Eurodia Industrie, Wissous, F; see Table II) as coupled to the conventional cationic membranes type CMX-Sb either in a laboratory-scale stack with an overall membrane surface area (A_{m}) of 0.2 m^2 (http://www.ameridia.com/html/fss.html) or in a pilot-scale one with $A_{\mathrm{m}} =$ 2.5 m^2 (Elmidaoui *et al.*, 2002), it was possible to overcome the earlier shortcomings, as shown in Table XIII. Further scaling-up in an industrial

TABLE XIII

MAIN RESULTS OF BEET SUGAR SYRUP DESALTING IN LABORATORY- AND PILOT-SCALE ED STACKS EQUIPPED WITH CMX-Sb AND AXE 01 MEMBRANES[a]

Beet sugar syrups	Laboratory plant		Pilot plant	Unit
Sucrose titre	30	50	55	°Brix
Temperature	50	50	60	°C
Current density	110	120	–	A/m^2
Voltage/cell	1	1	1.3	V
Conductivity decrease	70	70	75	%
Total cations removal yield	65	55	–	%
Ca^{2+} removal yield	60	35	65	%
Mg^{2+} removal yield	50	30	–	%
K^+ removal yield	75	75	86	%
Na^+ removal yield	25	45	75	%
Demineralization flux	3.5	4.5	–	$eq\ h^{-1}m^{-2}$
Current efficiency	90	90	–	%

[a] As extracted from Lutin (2000) and Elmidaoui *et al.* (2002), respectively.

plant consisting of two stacks EUR40 in series with capacity of 20 m^3/h yielded a demineralization degree of 60%, sugar loss less than 0.5%, a specific electric energy consumption of 1.1 kWh/m^3 for ion transport and pumping, and small consumption of chemicals for CIP of the order of 0.02 kg HCl/m^3 and 0.06 kg NaOH/m^3 (Lutin *et al*., 2002).

Despite this, the European sugar industry has been so far extremely reluctant to replace the rather environmentally polluting traditional technology with such a novel procedure. Moreover, even in this case a hybrid process combining MF and ED appears to be effective to minimize organic fouling, operate up to 60 °C, reduce waste formation and pollution load, improve sugar yields, reduce the volume of molasses, and save capital and operating costs.

Finally, the main by-product of molasses fermentation and distillation, that is, vinasse, where ash represents from 26% to 34% of dry matter, has to be demineralized to expand its usage in feed preparation. To this end, vinasse can be concentrated from about 6° to 20° Brix and then submitted to conventional ED processing (Milewski and Lewicki, 1988). For instance, at an 80% demineralization level, the K^+ content was completely removed, while the Na^+, Ca^{2+}, or Mg^{2+} content was decreased by about 52%, 40%, or 19%, respectively. De-ashed vinasse exhibited no change in the betaine content, while the fraction of total amino acids in the dry matter increased. The specific electric energy consumed per kg of ash removed was found to range from 10 to as high as 40 kWh/kg, while it was about 5 kWh/kg in the case of potassium removal from grape juice (Wucherpfennig, 1975).

G. FERMENTATION INDUSTRY

A sector where the application of ED is potentially interesting is that of the fermentation industry, especially when the main product of the microbial metabolism is an electrolyte. This may exert an inhibitory effect on cell growth and/or metabolite production in either its free or dissociated form. Alternatively, it may be dissolved in media rich of impurities that are to be removed via numerous and expensive purification steps.

By resorting to the so-called membrane recycle bioreactors (MBR) (Bubbico *et al*., 1997; Enzminger and Asenjo, 1986), continuous recycling of the culture broth through crossflow MF modules allows removal of the inhibiting metabolites, this helping to maximize cell density in the bioreactor, as well as bioproduct formation rate. Further ED treatment of MF permeates gives rise to two streams, a diluted one to be recycled back into the bioreactor, and a concentrated one to be supplementary refined.

Downstream processing may consist of several operations such as liming to precipitate the metabolite as the calcium salt, washing of the precipitate with water to remove soluble impurities, acidification using strong acids to convert the salt in its free acid form. The acidic liquor may be demineralized using IER, decolorized using active carbons, concentrated under vacuum, and finally crystallized.

Since the use of ED simplifies such a complex sequence of recovery techniques, ED is generally regarded as an environment-friendly alternative to the conventional bioproduct recovery processes.

Table XIV reviews a series of potential applications of ED to recover some microbial metabolites from the respective culture broths together with the microorganisms used and the main bottlenecks of conventional production processes, as well as their main references. For the most potentially relevant applications, more details are discussed later.

1. Acetic acid

Acetic acid (CH_3COOH) is a bulk commodity chemical with a world production of about 3.1×10^6 Mg/year, a demand increasing at a rate of +2.6% per year and a market price of US$0.44–0.47 per kg (Anon., 2001a). It is obtained primarily by the Monsanto or methanol carbonylation process, in which carbon monoxide reacts with methanol under the influence of a rhodium complex catalyst at 180°C and pressures of 30–40 bar, and secondarily by the oxidation of ethanol (Backus *et al*., 2003). The acetic fermentation route is limited to the food market and leads to vinegar production from several raw materials (e.g., apples, malt, grapes, grain, wines, and so on).

Despite only very large plants with capacities of (225–500) × 10^3 Mg/year are economically feasible (Backus *et al.*, 2003), there are strong market, economic, and energy benefits to develop novel fermentation processes to produce acetic acid in scalable, regional-sized plants (Office of Industrial Technologies, 2003) for the current high cost of methanol and the fact that concentrating acetic acid production in large-size plants makes contract selling prices greatly affected by costs of transportation and distribution networks.

Because of the higher yield coefficient for acetic acid on glucose and lower energy requirements of the anaerobic acidogenesis of glucose by *Clostridia* with respect to aerobic route using *Acetobacter aceti* (Cheryan *et al.*, 1997; Ghose and Bhadra, 1985), the anaerobic process is presently regarded as the method of choice to produce acetic acid as a chemical feedstock.

Figure 19 shows the flowchart of the integrated process for production and purification of fermentation-derived acetic acid, which was recommended by the Office of Industrial Technologies of the US Department of Energy (2003) as a viable pathway for commercialization of regional smaller scale acetic acid production plants. Of course, the economic profitability of such a process relies on appropriate mutants of acetogenic bacteria, as well as efficient membrane modules, capable, on one side, of maximizing the concentration of free acid in the exhausted fermentation broth and, by the other side, of minimizing acid recovery costs. To this end, novel pervaporation membranes with high ammonia permeability might enable pervaporation-assisted thermal cracking of ammonium acetate, thus allowing the aqueous solutions of ammonium hydroxide or free acetic acid to be recycled into the bioreactor as a nitrogen source or further purified, respectively (Office of Industrial Technologies, 2003). Moreover, the ED unit in Figure 19 would help not only to recover acetates from the generally dilute broths in which they are produced in ionized form (Chukwu and Cheryan, 1999), but also to keep a low acidic level and control the pH in the fermenting broth throughout the course of the fermentation (Nomura *et al.*, 1988, 1994). In both cases, the broth is to be microfiltered and then fed to the ED unit to be separated into an enriched salt product (concentrate) and a salt-depleted broth (dilute). Since the residual sugars and nutrients are retained in the dilute, its recycling into the bioreactor would enable material utilization and microbial acetate productivity to be maximized. Simultaneous recovery of acetic acid in the concentrate would facilitate its further separation and purification.

Even in the aerobic fermentation by *A. aceti*, the use of a combined automatic system (to remove continuously the acetic acid from the fermentation broth and keep the pH in the fermenter about constant by regulating the DC potential difference applied to the ED stack and ethanol concentration in

TABLE XIV

POTENTIAL APPLICATIONS OF ED TO RECOVER MICROBIAL METABOLITES FROM FERMENTATION MEDIA

Microbial metabolite	Microorganism used	Typical operating limits	Main references
Acetic acid	*Acetobacter aceti* *Clostridium thermoaceticum*	Product inhibition	Chukwu and Cheryan, 1999; Fidaleo and Moresi, 2005b; Nomura *et al.*, 1988, 1994
Acetic and propionic acid	*Propionibacterium shermanii*	Product inhibition	Zhang *et al.*, 1993
Citric acid	*Aspergillus niger* *Yarrowia lipolytica*	Complex recovery, environmental impact	Datta and Bergemamm, 1996; Ling *et al.*, 2002; Mancini *et al.*, 1995; Moresi and Sappino, 1998, 2000; Novalic *et al.*, 1995, 1996; Sappino *et al.*, 1996
Gluconic acid	*Aspergillus niger*	Complex recovery	Novalic *et al.*, 1997
Itaconic acid	*Aspergillus terreus*	Complex recovery	Kobayashi, 1967, 1978; Moresi and Sappino, 2000; Nakagawa *et al.*, 1975
2-Keto-L-gulonic acid	–	–	Oka *et al.*, 1998

Lactic acid	*Lactobacillus delbruekii*, *Lactococcus lactis*	Product inhibition, complex recovery	Boniardi *et al*., 1996; Boyaval *et al*., 1987; Fidaleo and Moresi, 2004; Gillery *et al*., 2002; Habova *et al*., 2001, 2004; Hongo *et al*., 1986; Ishizaki *et al*., 1990; Kim and Moon, 2001; Lee *et al*., 1998; Madzingaidzo *et al*., 2002; Moresi and Sappino, 2000; Nomura *et al*., 1987, 1988, 1991; Siebold *et al*., 1995; Vonktaveesuk *et al*., 1994; Xuemei *et al*., 1999; Yamamoto *et al*., 1993; Yen and Cheryan, 1993
Lysine and other amino acids	*Brevibacterium flavum, Corynebacterium glutamicum*	Product inhibition	Grib *et al*., 2000; Kikuchi *et al*., 1995; Lee *et al*., 2002b, 2003; Nomura *et al*., 1987
Malic acid	–	Complex recovery	Belafi-Bako *et al*., 2004; Sridhar, 1987
Propionic acid	*Propionibacterium acidipropionici*	Product inhibition	Boyaval and Corre, 1995; Boyaval *et al*., 1993; Fidaleo and Moresi, 2006; Weier *et al*., 1992
Pyruvic acid	*Escherichia coli*	Product inhibition	Zelic *et al*., 2004;
Succinic acid	–	–	Glassner and Datta; 1992

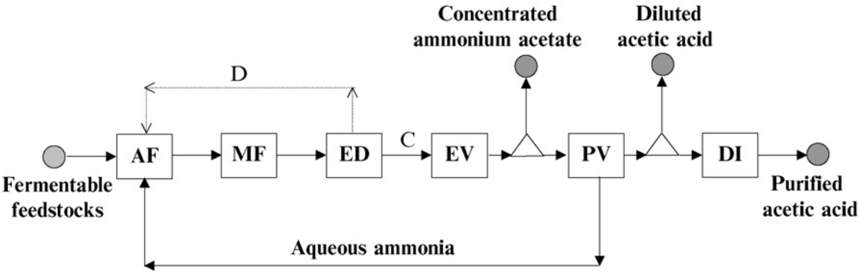


FIG. 19 Schematic flow diagram for the production and purification of fermentation-derived acetic acid, as modified from Office of Industrial Technologies (2003). Unit operation identification items: AF, anaerobic fermentation; DI, distillation; ED, electrodialysis; EV, evaporation; MF, microfiltration; PV, pervaporation-assisted thermal cracking.

the fermenting medium) resulted in acetate productivities (2.13 g/h) about 1.35 times greater than those (1.58 g/h) obtained in fermentation trials without any pH control and practically no effect on the yield coefficient for acetic acid on ethanol (1.13–1.18 g/g) (Nomura *et al*., 1988).

The same combined fermenter-ED system was used to improve simultaneous excretion of acetic and propionic acids by *Propionobacterium shermanii* (Zhang *et al*., 1993), their enhancement factors with respect to the conventional fermentation unit being of the order of 1.3 and 1.4, respectively.

2. *Citric acid*

The global market of citric acid ($C_6H_8O_7$) is about 1.4×10^6 Mg equivalent to US$5.3 billion and represents circa 70% of all food acidulants utilized in the field of foods and pharmaceuticals (http://www.foodproductiondaily.com/news/ng.asp?id=63089). It is mainly produced by high citric acid-yielding strains of *Aspergillus niger* by submerged-culture fermentation of production media based on molasses or other glucose/sucrose sources. In spite of the interest in citric acid production by yeast grown submerged in sugar- or hydrocarbon-based media to overcome the main disadvantages of the traditional mould fermentation (i.e., high sensitivity to trace metals and low production rates), no yeast-based process is known to be operating worldwide. In fact, among the fermentation plants using the Japanese industrial know-how (e.g., Takeda Chemical Industries) that constructed at Southport (North Carolina, USA) was shut down in 1982 after 3–4 year operation, while the Liquichimica plant (Saline, Italy) never came into operation (Moresi and Parente, 1999).

Once mycelia have been separated via continuous filtration from exhausted production media, citric acid may be recovered by using three different methods, such as *direct crystallization* upon concentration of the filtered liquor, *precipitation* as calcium citrate tetrahydrate, or *liquid extraction*. Since molasses are extremely rich in impurities, direct crystallization cannot be applied unless very refined raw materials, such as sucrose syrups or crystals, are used. The precipitation process (that is based on subsequent addition of sulfuric acid and lime to clarified fermentation broths) is used by the great majority of world citric acid manufacturers, including Archer Daniels Midland Co. (ADM) in the United States. Liquid extraction with mixtures of trilaurylamine, n-octanol, and C_{10} or C_{11} isoparaffin was used by Pfizer Inc. in Europe and Bayer Co. (formerly Haarmann & Reimer Co., subsidiary of Miles) in the Dayton (OH, USA) and Eikhart (IN, USA) plants only (Moresi and Parente, 1999), even if such plants might have been shut down in 1998.

To overcome such a drawback, that is, the formation and disposal of enormous amounts of liquid effluents (their Chemical Oxygen Demand being about 20 kg/m^3) and solid by-products (i.e., about 0.15 kg of dried mycelium and 2 kg of $CaSO_4.2H_2O$ per kg of monohydrated citric acid), several process alternatives have been so far suggested to minimize the overall environmental impact of this process (Moresi and Parente, 1999).

Citric acid recovery by ED was early proposed by Voss in 1986 (Ling *et al*., 2002). The specific energy consumption (ε) depended on the electromembranes used and was about 1.7–2 or 0.3–0.9 kWh/kg of citrate recovered in the case of bipolar (Novalic *et al*., 1996) or monopolar (Datta and Bergemann, 1996; Ling *et al*., 2002; Mancini *et al*., 1995; Novalic *et al*., 1995; Sappino *et al*., 1996) membranes, respectively.

ED appears to be an inefficient method to recover free citric acid because of its low electric conductivity (Novalic *et al*., 1995). As it is converted into the monovalent (at pH ca. 3), divalent (at pH ca. 5), or trivalent (at pH about 7) citrate anion, there is a significant increase in the electric conductivity (χ), the latter increasing from 0.95 to 2.18 and to 3.9 S/m, respectively, in the case of an aqueous solution containing 50 kg/m^3 of citric acid equivalent (Moresi and Sappino, 1998). By increasing the pH from 3 to 7, ε reduced about eight times, the solute flux (J_B) practically doubled, while the overall water transport (J_W) increased 3–4 times. The latter partly counterbalanced the greater effectiveness of the electrodialytic concentration of citric acid at pH 7 with respect to that at pH 3. Table XV presents a summary of the effect of current density (j) on the main performance indicators of the electrodialytic recovery of the monovalent, divalent, or trivalent ionic fractions of citric acid (Moresi and Sappino, 1998). All the mean values or empirical correlations of the earlier indicators were useful to evaluate the economic feasibility of this separation technique (Moresi and Sappino, 2000).

TABLE XV

ELECTRODIALYTIC BATCH RECYCLE RECOVERY OF A FEW SODIUM SALTS OF LACTIC, ITACONIC, AND CITRIC ACIDS FROM AQUEOUS SOLUTIONS AT DIFFERENT pH VALUES AND 33°C[a,b]

	Mean values or empiric correlations					
	Citrate			Lactate	Itaconate	
Indicator	pH = 3	pH = 5	pH = 7	pH = 5	pH = 6	Unit
ζ	0.90 ± 0.08	0.90 ± 0.04	0.97 ± 0.02	1.06 ± 0.03	1.02 ± 0.04	dimensionless
Ω	0.09 ± 0.02	0.41 ± 0.03	0.50 ± 0.01	0.62 ± 0.07	0.61 ± 0.05	dimensionless
ε	$0.33\,j$	$0.064\,j$	$0.040\,j$	$0.0306\,j^{0.48}$	$0.00016\,j^{1.65}$	kWh/kg
J_B	$0.0084\,j$	$0.018\,j$	$0.016\,j$	$0.0026\,j$	$0.0020\,j$	kg m^{-2} h^{-1}
J_W	0.176 ± 0.004	$0.050\,j$	$0.050\,j$	$0.0083\,j$	$0.0067\,j$	dm^3 m^{-2} h^{-1}

[a] Mean values or empirical correlations between each performance indicator and current density (j), expressed in A/m^2.

[b] Moresi and Sappino (1998, 2000).

Note: Solute recovery efficiency, ζ; Faraday efficiency, Ω; specific energy consumption, ε; solute flux, J_B; and average water flux, J_W.

The effectiveness of this ED process increases with temperature, being presently limited by the maximum operating temperature (35°C) of the AMV and CMV electromembranes used (Table II).

Figure 20 shows a schematic of a novel membrane-integrated process for citric acid production from glucose syrups by *Yarrowia lypolitica* ATCC 20346, based on prolonged fed-batch fermentation carried out in a stirred bioreactor coupled to a MF unit equipped with tubular ceramic membranes, and disodium citrate recovery from MF permeates by ED (Moresi, 1995).

A combined system consisting of an anion exchanger and a two-compartment ED stack using bipolar and cationic membranes (Figure 8B) was patented by Morita *et al.* (1996) to recover citric acid and NaOH with reduced or nil consumption of reagents (H_2SO_4, lime) and no formation of residues ($CaSO_4$). After centrifugation to remove mycelia, the culture broth was fed to a column containing a weakly basic anion-exchange resin (Diaion WA-30; Mitsubishi Chem. Corp., Tokyo) to adsorb citric acid. By washing sequentially the column with equal volumes of demineralized water and aqueous NaOH (1 kmol/m^3), it was possible to regenerate the column, as well as to recover the sodium salts of citric acid by collecting the fractions at pH values ranging from 3.0 to 6.0. Such fractions were fed into the acid compartments of the aforementioned ED stack arrangement, thus resulting in an overall citric acid recovery yield of 96%. Further decolorization by activated charcoal, concentration, and crystallisation ensued citric acid crystals of 99.5% purity (Morita *et al.*, 1996).

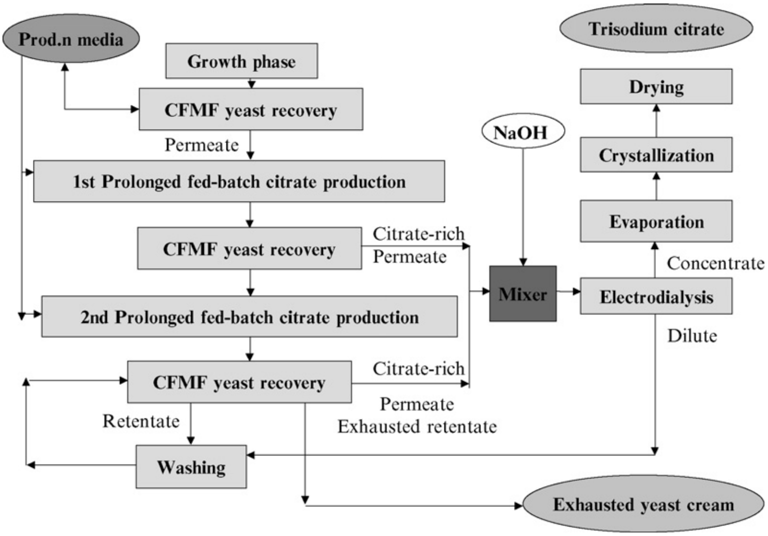


FIG. 20 Flow sheet of a novel integrated membrane process for citric acid production from glucose syrups by *Yarrowia lipolytica*, as proposed by Moresi (1995).

3. *Itaconic acid*

Itaconic acid (HOOC–CH=CH–COOH, $C_4H_4O_4$) is used as monomer or comonomer for plastics, resins, synthetic fibres, and elastomers (Milson and Meers, 1985) and it is produced by submerged culture fermentation with *Aspergillus terreus* in a medium containing molasses as the sugar source at 32–40°C and pH of 1.8–4.0 under 0.25–0.5 volumes of air per volume of medium per minute for 48–72 hour (Milson and Meers, 1985; Roehr and Kubicek, 1996). Use of ED was suggested to enhance the mycelial itaconate productivity in wood waste- (Kobayashi, 1967, 1978; Nakagawa *et al.*, 1975), pretreated beetjuice-, or molasses- (Nakagawa *et al.*, 1991) based media. More recently, Moresi and Sappino (2000) assessed the effect of *j* on the main performance indicators (Table XV) and specific recovery costs as a function of plant size.

4. *Lactic acid*

Lactic acid (CH_3–CHOH–COOH) is commonly used as a food additive for flavor and preservation. It is also converted into a polylactide polymer, which represents one of the first commercial applications of biodegradable polymers. It is produced by chemical synthesis or fermentation using lactococci, mesophilic lactobacilli (*Lactobacillus casei* subsp. *casei, Lb. amylophilus*), or thermophilic streptococci (*Streptococcus thermophilus*), these strains producing pure L-(+)lactic acid, the only enantiomer metabolized by humans (Moresi and Parente, 1999).

The global capacity of lactic acid is around 250,000 Mg/year and about 80% of the product is produced with the liquor resulting from corn wet milling (Anon, 2001b), since the use of the product chemically synthesized is restricted. China has more than 70 lactic acid producers with a total capacity of around 30,000 Mg/year (Anon, 2001b).

Lactic acid fermentation is hampered by two main bottlenecks (Yen and Cheryan, 1993). Undissociated lactic acid acts as a noncompetitive inhibitor for growth and lactic acid production by diffusing through the membrane and decreasing intracellular pH (Yen *et al.*, 1991). Thus, the pH is controlled at 5–6.5 by automatic addition of NaOH, Na_2CO_3, or NH_4OH. By referring to lactic acid production from yeast-extract enriched glucose-based media by *Lactobacillus delbruckii* (Yen *et al.*, 1991), the specific cell growth and lactic acid production rates were found to be practically independent of undissociated lactic acid concentration for concentrations lower than 0.12 kg/m^3. On the contrary for greater concentration values, both rates exhibited an almost linear decrease.

Batch fermentations result in high product concentration (120–150 kg/m^3) but in low productivity (2 kg m^{-3} h^{-1}). Dramatic improvements in productivity (20–80 kg m^{-3} h^{-1} in laboratory- and pilot-plant experiments) were obtained by using cell recycle via MF or immobilized cells, at the expense of lactate concentration in the effluent (usually lower than 50 kg/m^3).

Lactic acid recovery from fermentation broths, as well as its refining, is difficult owing to the high solubility of its salts, and significantly affects its downstream processing costs. The traditional process involves precipitation of calcium lactate and regeneration of lactic acid by addition of sulfuric acid followed by further purification steps (IE and decolorization). This gives rise to about 1 kg of $CaSO_4 . 2H_2O$ per kg of lactic acid, thus resulting in enormous amounts of crude calcium sulfate (circa 0.36×10^6 Mg/year) that are to be dumped as industrial wastes (U.S. Department of Energy, 1999). Alternative processes are solvent extraction (Yabannavar and Wang, 1991), adsorption (Kaufman *et al.*, 1994), and direct distillation (Cockrem and Johnson, 1993).

Combined use of lactate fermentation and ED separation has been proposed to overcome the main drawbacks of this fermentation process, that is, low microbial acidic productivity and expensive downstream processing of lactic acid fermentation broths (Boyaval *et al.*, 1987; Hongo *et al.*, 1986;

Ishizaki *et al.*, 1990; Kim and Moon., 2001; Lee *et al.*, 1998; Madzingaidzo *et al.*, 2002; Nomura *et al.*, 1987b, 1991).

As an example, Nomura *et al.* (1991) made use of a combined system (consisting of a fermenter, F, a MF module, and an ED stack), to recover first the microbial biomass from the culture broth by MF and second the lactate from the resulting MF permeate by ED. By recycling the cell-rich MF retentate, as well as the residual sugar- and nutrient-rich ED diluate, back into the bioreactor, it was possible to maximize material utilization and microbial lactate productivity. Then, simultaneous recovery of the lactic acid in the ED concentrate would also relieve the environmental impact of the conventional lactic acid recovery process. In a previous study carried out without the MF module (Ishizaki *et al.*, 1990), the experimental increase in microbial lactic acid production rate was less than expected as a consequence of cell damage and/or adhesion to the anionic membranes as the whole culture broth was recirculated through the ED stack. As referring to the lactate fermentation from glucose by *Lactococcus lactis* IO-1 in the combined F-MF-ED system, after 38 hour cell concentration (2.89 kg/m^3) and living cell count (4.8×10^{15} cell/m^3) were, respectively, circa 1.8 and 1.6 times greater than those observed during a conventional fermentation, thus involving greater glucose consumption and lactate production rates.

The performance of the F-MF-ED system was also assessed in the case of lactate fermentation from xylose (Nomura *et al.*, 1988). Starting with 50 kg of xylose per m^3, the conventional or combined system allowed full exhaustion of the carbon source after 60 or 32 hours, respectively. By further increasing the initial xylose concentration to 80 kg/m^3, both systems resulted in less (50 kg/m^3) or more (75 kg/m^3) consumption of xylose, respectively. Moreover, the simultaneous removal of microbial metabolites (lactate and acetate) via ED increased both lactate production and xylose consumption rates.

Simultaneous L-lactic acid fermentation (by *Rhizopus oryzae* immobilized in calcium alginate beads) and separation was carried out using a three-phase fluidized-bed bioreactor as a fermenter (F), an external electrodialyzer as a separator, and a pump to recycle the fermentation broth between the bioreactor and the separator. In this way, the experimental specific lactate productivity and yield practically coincided with those obtained in the $CaCO_3$-buffered fermentation process (Xuemei *et al.*, 1999), thus confirming the capability of the combined system to alleviate product inhibition without any addition of alkali or alkali salts. It was also shown that the adoption of ED-F for the production of inoculum reduced variability in inoculum quality, thus shortening the length of the lag phase of L-lactate production practically to zero as compared to that observed using an inoculum conventionally cultured for 24 hour (Yamamoto *et al.*, 1993). In the case of lactic acid production from glucose by *L. lactis* IO-1, about a double increase in lactate production rate was achieved using periodic ED in place of a combined F-MF-ED system (Vonktaveesuk *et al.*, 1994).

A two-stage ED process was proposed to recover lactic acid from model solutions and from fermentation media (Habova *et al.*, 2001, 2004). The broth was ultrafiltrated, decolorized by flowing through a granulated active charcoal-filled column, concentrated more than 2.5 times to 110–175 kg of sodium lactate per m^3 via ED using monopolar membranes, and finally separated into two streams rich in sodium hydroxide and free lactic acid (ca. 150–160 kg/m^3), respectively, using bipolar membranes Neosepta® (Tokuyama Corp., Japan) with an overall energy consumption of about 1.6 kWh/kg of lactate transported. A similar procedure was tested by Madzingaidzo *et al.* (2002), thus yielding almost congruent results in terms of average energy consumption in the 1st (0.6 kWh/kg) and second (0.6–1.0 kWh/kg) stage and lactate (15% w/w) or free lactic acid (16% w/v) concentration in the concentrated stream flowing out of them, respectively. In the optimal operating conditions current efficiency in the monopolar and bipolar ED was about 90%. Moreover, during the electrodialytic purification significant reduction in color and minerals in the free lactic acid solution was obtained, while the glucose and acetic acid contents were reduced to less than 1 kg/m^3.

On the contrary, a more efficient splitting of sodium lactate into lactic acid (0.96 kg/kg) and sodium hydroxide (0.93 kg/kg) was obtained using a single step three-compartment bipolar ED process, as that shown in Figure 6A, and no pretreatment of the fermentation broth (Kim and Moon, 2001).

The performance of the ED recovery of sodium lactate from model solutions was mathematically described by several authors (Boniardi *et al.*, 1996; Fidaleo and Moresi, 2004; Yen and Cheryan, 1993). It was found that the permeation flux of lactate was independent of the presence of lactose and glucose in culture medium and that the fluxes of both sugars were practically negligible (Yen and Cheryan, 1993). By using the performance indicators reported in Table XV, Moresi and Sappino (2000) estimated that the ED recovery of sodium lactate was less expensive than that of disodium itaconate or trisodium citrate.

Although promising prospects for lactate recovery by monopolar (Moresi and Sappino, 2000) or bipolar (Siebold *et al.*, 1995) ED have been presented, a resistance to embrace this technology still persists and just a fermentation industry in France seems to have adopted such a technology (Gillery *et al.*, 2002).

5. *Malic acid*

L-Malic acid (HOOC–CH_2–CHOH–COOH) for use in the pharmaceutical industry is manufactured by conversion of fumaric acid by the intracellular enzyme fumarase produced by various microorganisms. The excess fumaric acid is easily separated by crystallization after concentration of the mother solution. Further addition of lime allows malic acid to be separated as calcium malate within a bioreactor crystallizer system. By adding diluted sulfuric or oxalic acid, the salt is split into free malic acid and calcium sulfate or oxalate, the latter being removed by filtration (Mourgues *et al.*, 1997).

To simplify such a complex procedure, Sridhar (1987) suggested to make use of a single six-compartment ED stack, as schematically shown in Figure 21.

Fumaric acid crystals are dissolved in water and fed to compartment Z2, where hydrogen ions (H^+) are attracted by the cathode, pass through the cationic membrane, and accumulate into the cathodic compartment (Z1). On the contrary, fumarate ions (Fum^{2-}), direct toward the anode, permeate through the anionic membrane, and accumulate into the compartment Z3, where they are neutralized by the ammonium ions (${NH_4}^+$) arriving from compartment Z4. Malate ions (Mal^{2-}) migrate into compartment Z5, where they recombine with the hydrogen ions (H^+) coming from the anodic compartment (Z6), thus yielding the final product (malic acid) of this process. The ammonium fumarate is circulated through the bioreactor (R) to be enzymatically converted into ammonium malate. The electrode compartments are washed using acidic solutions and continuously refilled with water, the electrolysis of which generates gaseous hydrogen (H_2) or oxygen (O_2) at the cathode or anode, respectively.

In this way, it would be possible to convert electrodialytically fumaric acid into ammonium fumarate. This in turn may be enzymatically transformed into ammonium malate, which might finally be ED freed into malic acid with no reagent consumption and by-product formation, and minimum product loss.

This procedure was recently confirmed by Belafi-Bako *et al.* (2004).

6. *Propionic acid*

Propionic acid (CH_3CH_2COOH) is produced using mainly the oxo process (about 200,000 Mg), which involves reacting ethylene and carbon monoxide to produce propionaldehyde, to be further oxidized in the presence of cobalt or manganese ions at 40–50°C (Anon., 2002). About 45% of the overall consumption of propionic acid is used as such or as ammonium propionate

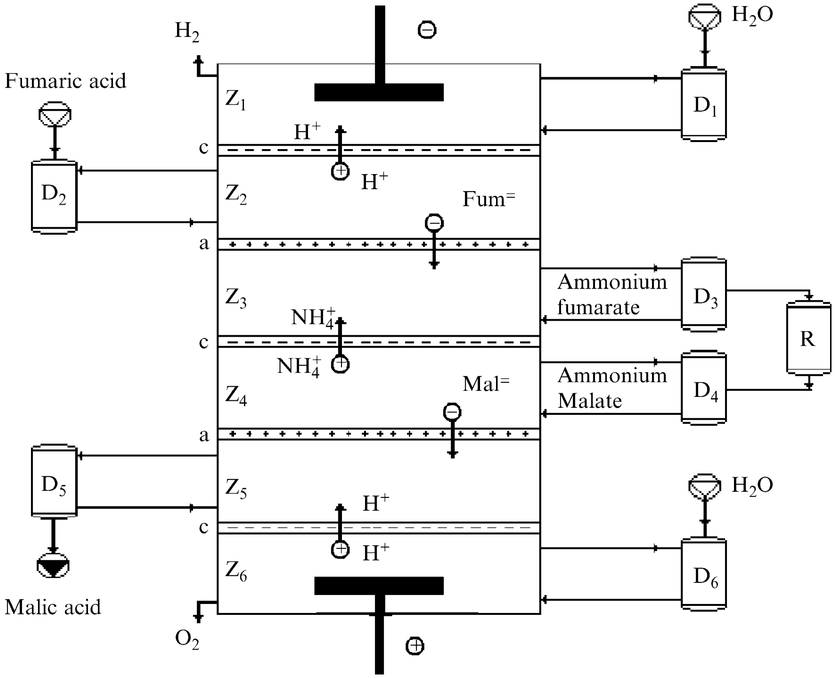


FIG. 21 Schematic diagram for the production of L-malic acid from fumaric acid using a six-compartment (Z_1–Z_6) ED stack composed of anionic (a) and cationic (c) membranes, as extracted from Sridhar (1987). As ammonium fumarate is formed, it is enzymatically converted into ammonium malate in an external bioreactor (R). The combined system is also provided with a series of storage tanks for the acidic cathode-(D1) and anode-(D6) rinsing solutions, raw materials (D2), ammonium fumarate (D3), ammonium malate (D4), and final product (D5).

to prevent mould in animal feeds; 21% is converted into sodium and calcium propionates to preserve baked goods and cheeses; 19% is used to produce diethyl ketone (DEK), that is, an intermediate in the manufacture of herbicides, such as pendimethalin; circa 11% is converted into cellulose acetate-propionate plastics (as moulding compounds for toothbrush handles, other brush handles, and eyeglass frames), and the remaining 4% into pharmaceuticals and propionate esters for solvents, flavors, and fragrances.

Propionic acid might be also produced by fermentation of *Propionibacterium acidipropionici*, thus providing an attractive alternative that can also meet consumer's demand for natural preservatives used in the food industry. However, conventional batch propionic acid fermentation suffers from low productivities (< 1 kg $m^{-3}h^{-1}$), low product concentrations (< 50 kg/m^3), low-propionic acid yield (0.548 g/g of glucose) due to the formation of acetic acid (0.222 g/g) as a main by-product and slow microbial growth as strongly inhibited by propionic acid and acidic pH (Boyaval and Corre, 1995; Moresi and Parente, 1999).

A great deal of research work has been carried out to enhance bioreactor productivity (2–14 kg $m^{-3}h^{-1}$) using cell recycle via membrane processing (Boyaval and Corre, 1987; Boyaval *et al.*, 1994) and recovering propionic acid by monopolar or bipolar ED (Boyaval *et al.*, 1993; Weier *et al.*, 1992; Zhang *et al.*, 1993).

To avoid the cosynthesis of acetate by *P. thoenii*, it was suggested to replace conventional carbon sources with glycerol, thus obtaining a theoretical yield of 0.804 g of propionic acid per g of glycerol and no acetic acid (Boyaval and Corre, 1995; Himmi *et al.*, 2000).

In the circumstances, it seems to be possible to readdress industrial manufacturers toward the fermentation route by resorting to an integrated process involving appropriate mutants of *Propionibacterium* spp., glycerol-based media, as well as efficient membrane modules capable of keeping the concentrations of free acid or bacteria in the culture medium to the minimum or maximum level, respectively. To this end, an ED unit would help not only to recover sodium propionate from the generally dilute broths in which it is produced in ionized form (Weier *et al.*, 1992), but also to keep a low acidic level and control the pH in the fermenting broth throughout the course of the fermentation (Zhang *et al.*, 1993). Generally, the broth is to be microfiltered and then fed to the ED unit to be separated into an enriched salt product (concentrate) and a salt-depleted broth (dilute). Since the residual sugars and nutrients are retained in the dilute, its recycling into the bioreactor would enable material utilization and microbial propionate productivity to be maximized. Use of bipolar membranes would also allow the aqueous solutions of sodium hydroxide or free propionic acid to be recycled into the bioreactor for the pH control or further purified, respectively (Boyaval *et al.*, 1993).

Boyaval *et al.* (1993), Weier *et al.* (1992), and Zhang *et al.* (1993) attempted to optimize the electrodialytic recovery of propionate from model or real solutions by resorting to a few performance indicators (i.e., current efficiency, solute recovery yield, solute and water fluxes). Despite such parameters were found to be dependent on the feed solutions used, that is, model sodium propionate and/or sodium acetate media and real fermentation broths, Weier *et al.* (1992) were able to estimate the membrane surface area required to guarantee low propionate levels (0.10–0.32 kmol/m^3) during the fermentation as a function of the fermenter size.

7. *Pyruvic acid*

Fed-batch production of pyruvic acid [$CH_3COCOOH$] from an engineered strain (*Escherichia coli* YYC202) was optimized by resorting to ED to prevent potential product inhibition in the bioreactor (Zelic *et al*., 2004). In this way, by continuous separation of pyruvate from the fermentation medium, high values of the pyruvate-to-glucose molar yield (1.78 mol/mol), volumetric productivity (145 kg $m^{-3}day^{-1}$), and pyruvate concentration (79 kg/m^3) were achieved by the repeated fed-batch mode.

8. *Succinic acid*

A two-stage ED process was also proposed to recover succinic acid [HOOC $(CH_2)_2COOH$] from sugar- and triptophane-based fermentation media (Glassner and Datta, 1992). The broth was previously concentrated via ED using monopolar membranes and then separated into sodium hydroxide- and free succinic acid-rich streams using bipolar membranes. Further removal of sodium cations and sulfate anions was achieved using weakly acid and -basic IER.

9. *Lysine and other amino acids*

Lysine is an essential bibasic amino acid to support growth in children and general well-being in adults. It is also quite an important ingredient in feed mixes, especially for pigs and chickens. It is mainly produced by submerged fermentation using overproducing mutants of *Corynebacterium glutamicum* that are able to excrete up to 100 kg of lysine per m^3 at the end of fermentation, and commercialized as L-lysine hydrochloride. The process is generally carried out by intermittent feeding of the carbon source to prevent sugar inhibition on cell growth and lysine production rates.

Ajinomoto and BASF are leading lysine manufacturers. For instance, Ajinomoto is expected to expand its global lysine capacity to 300,000 metric tons by 2005 (http://static.highbeam.com/c/chemicalweek/january262000/ajinomotoraiseslysineproductionworldwide/).

Nomura *et al*. (1987a) attempted to minimize product inhibitory effect on the aspartate kinase step in lysine biosynthesis and enhance L-lysine production from *Brevibacterium flavum* QL-5 using a combined ED-F system. However, lysine production was not statistically different from that obtained in diffusion dialysis fermentation and about 20% greater than that achieved during conventional fermentation, thus making practically ineffective such a use of ED.

Desalting of lysine-rich fermentation broths by monopolar ED appears to be much more rewarding. To mitigate anionic membranes sensitivity to fouling, Lee *et al.* (2002b, 2003) resorted to pulsed electric field with the half-wave power and suggested the use of pulse power as an effective CIP method during ED of fermentation media.

A typical three-compartment ED stack using bipolar, cationic, and anionic membranes (Figure 8A) was patented by Mani (2000) to produce lysine hydrochloride. By feeding the salt compartments with a salt (e.g., NaCl, KCl, or LiCl) solution, the base and acid ones with water and a lysine-rich solution, respectively, the salt can be split into an alkali and hydrochloric acid. The latter reacts with lysine, thus yielding the amino hydrochloride.

Kikuchi *et al.* (1995) made use of an ED stack composed of Selemion-CMV and -AMV electromembranes (Table II) to separate almost completely a mixture of amino acids, that is, glutamic acid, methionine, and lysine. In this way, while methionine was not affected by the voltage applied, glutamic acid or lysine was found be transported across the anion- or cation-exchange membranes, respectively.

The recovery of phenylalanine from an industrial process stream was carried out using a conventional ED stack (Grib *et al.*, 2000). A preliminary soaking of such membranes in a bovine serum albumin solution for 2 hour allowed the reduction of phenylalanine loss to less than 5% and achievement of an average current efficiency of 98%. Such a process was also successful in removing 98% of Na_2SO_4 and $(NH_4)_2SO_4$.

H. OTHER FOOD INDUSTRIES

A few novel ED applications in the food sector have been reported in the literature and are generally aimed at desalting some food extracts.

For instance, the acidity of steam-stripped coffee extracts was reduced by about 50% using ED against a stream of 0.3% KOH at a current density of about 108 A/m^2 at 38 °C (Husaini, 1982).

The mussel cooking juice was desalted using two alternative technologies, that is, ED and diafiltration, thus resulting in about 80% or 77% demineralization degree with no or significant loss of flavor, respectively (Cros *et al.*, 2003). Alternatively, the centrifuged juice was previously desalted by ED and then concentrated by RO. Whereas the permeate might be disposed of without further depuration treatments, the retentate presented a sensory profile slightly different from that of unprocessed mussel cooking juice, but with its native characteristic aroma, thus making it useful as mussel flavor extract for human or pet food industries (Cros *et al.*, 2004).

ED was also suggested to deacidify liquorice extracts, containing 4–20% glycyrrhizic acid and 10–40% dry matter, or to desalt the glycyrrhizin-free juice recovered after acidification (Bozzi *et al.*, 1997).

Multistage ED stacks were also proposed to separate racemic mixtures of D,L-tryptophan in combination with a chiral selector (i.e., α-cyclodextrin). Despite the low selectivity (1.12) of such selector, the enantiomeric excess difference was found to range from 14% to 99% using ED stacks composed of 20 to 250 compartments, respectively (van der Ent *et al.*, 2002).

Genders and Hartsough (1999) patented an electrochemical method to recover ascorbic acid from an ascorbate salt and an inorganic salt (NaCl) without cogeneration of a waste salt stream and maintaining a high electric conductivity. The ascorbate-rich feed is dissociated into ascorbate anions and Na^+ cations under the influence of an electric field, while water splitting occurs in virtue of the bipolar membranes. As shown in Figure 8B, the hydrogen ions combine with the ascorbate anion to form ascorbic acid, while Na^+ cations migrate through the cationic membrane into the base compartment to combine with the hydroxyl ion to form the coproduct base (e.g., NaOH). The ascorbic acid is then crystallized and recovered.

IV. MATHEMATICAL MODELING OF AN ED DEVICE

To design or optimize an ED process several parameters are to be taken into account, namely stack construction and spacer configuration, operation mode, membrane perm-selectivity, feed and product concentration, flow velocities, current density and voltage applied to the electrodes, recovery rates, and so on.

The MS equation represents the simplest mathematical tool for linking the flux of a generic species through the membrane with its interfacial concentrations at the membrane left and right sides, as well as with the external electrical voltage applied to the ED electrodes (Krishna and Wesselingh, 1997). To overcome the main problem in the application of the MS mass transfer model to ED processes, that is, the large number of species diffusivities in the free solution and membrane phase (van der Stegen *et al.*, 1999), NP relationship is largely used to describe diffusion and electromigration contributions to ion transport in IEM (Bailly *et al.*, 2001; Boniardi *et al.*, 1996, 1997; Fidaleo and Moresi, 2004, 2005a; Ibanez *et al.*, 2004; Lee *et al.*, 1998, 2002d; Nikonenko *et al.*, 2002, 2003; Yen and Cheryan, 1993).

The basic mathematical model consists of water and solute mass balances in the concentrating and diluting tanks that are to be coupled with the solute—Eq. 11—and water—Eqs 12 and 13—mass transfer equations and voltage equation—Eq. 18—for the ED loop concerned.

Assuming perfect mixing in each compartment of the membrane pack and reservoir of the ED unit shown in Figure 9, the solute concentration in any of them is uniform and equal to that of the outlet stream. Therefore, by assuming pseudo-steady state conditions in any compartment, the differential solute and water mass balances in the diluted (D) and concentrated (C) reservoirs can be written as follows:

$$\frac{\mathrm{d}(n_{\mathrm{BC}})}{\mathrm{d}\theta} = -\frac{\mathrm{d}(n_{\mathrm{BD}})}{\mathrm{d}\theta} = J_B a_{me} N_{\mathrm{cell}} \tag{28}$$

$$\frac{\mathrm{d}(n_{\mathrm{WC}})}{\mathrm{d}\theta} = -\frac{\mathrm{d}(n_{\mathrm{WD}})}{\mathrm{d}\theta} = J_{\mathrm{W}} a_{\mathrm{me}} N_{\mathrm{cell}} \tag{29}$$

where n_{Bk} and n_{Wk} are the instantaneous solute and water mass in the k-th reservoir; θ is the process time; N_{cell} the overall number of cell pairs; and a_{me} the effective membrane surface area as viewed by the electrodes themselves.

Thus, any ED unit design or optimization exercise relies on quite a great number of engineering parameters, such as ion transport numbers in solution (t^+ and t^-) and electromembranes (t_a^-, t_c^+); effective solute (t_s) and water (t_{W}) transport numbers; solute (L_{B}) and water (L_{W}) transport rates by diffusion; effective membrane surface area (a_{me}); membrane surface resistances (r_a, r_c); solute mass transfer coefficient (k_m); and limiting current density (j_{lim}). These can be determined by independent experiments, tabulated data, or existing correlations.

In previous work (Fidaleo and Moresi, 2005a) a five-step sequential procedure was set up to assess such parameters by independent experiments. It mainly consisted of the following independent tests:

1. Zero-current leaching, osmosis, and dialysis tests to determine L_{B} and L_{W}.
2. Electroosmosis tests to estimate t_{W}.
3. Desalination tests to establish t_s.
4. Current-voltage tests to determine the limiting current intensity (I_{lim}), ion transport numbers ($t_a{}^-$, $t_c{}^+$), and surface resistances (r_a, r_c) in anionic and cationic membranes, as well as solute mass transfer coefficient (k_m).
5. Validation tests to assess the accuracy of all the parameters given earlier.

In this way, it was possible to extend the range of application of the NP equation from NaCl concentrations smaller than 0.1 (Krishna, 1987) or 0.5 (Lee *et al.*, 2002d) kmol/m^3 to about 1.7 kmol/m^3 (Fidaleo and Moresi, 2005a). Further details were reported elsewhere (Fidaleo and Moresi, 2005a).

As a result of a few parameter sensitivity analyses carried out in the case of the ED recovery of some sodium salts of hydrogen chloride (Fidaleo and Moresi, 2005a), lactic (Fidaleo and Moresi, 2004), acetic (Fidaleo and

Moresi, 2005b), or propionic (Fidaleo and Moresi, 2006) acids from model solutions, it is worth pointing out the following:

1. The solute and water transport numbers in the electromembranes reported in the literature may be accurate enough to predict the solute concentrations in C and D tanks and may need no extra experimental trials.
2. The contribution of solute diffusion (L_B) at zero current is usually negligible, that is, within the experimental error deviation band, with respect to that of electromigration. On the contrary, that of solvent diffusion (L_W) increases with the solute concentration difference at the membrane sides, especially at low current densities. It should be taken into account to reproduce accurately the experimental solute concentrations in the concentrate, especially at the end of ED recovery processes performed at low current densities (Fidaleo and Moresi, 2005a).
3. The solute mass transfer coefficient (k_m) in ED stacks approximately varies with the square root of the liquid superficial velocity (v_S) in agreement with the correlations reported in Table III, even if they can differ from those predicted within a ±30% deviation band because of the different cell and spacer configuration used.
4. As far as the overall potential drop (E) is concerned, the contribution of solute polarization, namely the electric resistance (R_f) and junction potential difference (E_j) across any boundary layer, may be neglected. On the contrary, the Donnan potential difference (E_D) in any cell pair, which behaves as a DC generator with inverted polarities with respect to those of the external DC generator (Figure 9), has to be accounted for as the solute concentration difference at both sides of the anionic and cationic membranes increases:

$$E_D = 2t_s \frac{R_G T_K}{F} \ln\left(\frac{c_{BD}}{c_{BC}}\right) \tag{30}$$

5. The ohmic resistances of the bulk solutions in the concentrating (C), diluting (D), or ERS compartment can be estimated via the second Ohm's law, as reported in Table IV.
6. The effective surface resistances of the anionic (r_a) and cationic (r_c) membranes are generally greater than those provided by the manufacturer (Table II), these being measured in a bridge circuit using alternating current. As a rule of thumb, such values are to be multiplied by 1.75 to express approximately the membrane surface resistance to DC (Davies and Brockman, 1972). Moreover, the membrane surface resistances may be regarded as

independent of the solute concentration (Lee *et al.*, 2002d). Both statements were confirmed by Fidaleo and Moresi (2005a).

7. Knowledge of the effective membrane surface area (a_{me}) is of paramount importance for a safe transfer of the data collected in a laboratory- or pilot-scale plant into an industrial-scale one. In previous work (Fidaleo and Moresi, 2004, 2005a,b), a_{me} was found to be about two-thirds of the geometrical membrane surface area (a_{mg}) and just 10% greater than the exposed surface area of electrodes (a_{ERS}). The latter may in principle be different from the former owing to the fact that the ion flow pattern starts in the direction orthogonal to the electrode surfaces and tends to diverge to maximize membrane area utilization and consequently minimize the electrical resistance of solutions fed in C and D compartments (Davies and Brockman, 1972). This is apparently in line with the empirical rule of overdesigning the geometrical membrane surface area by a correction factor of the order of 70% to account for the shadow effect of the spacer (Lee *et al.*, 2002d), since such an effect is nonlinearly related to the spacer-strand thickness and density (Turek, 2002). Thus, it is highly recommended to assess the effective surface area to assess the real limiting current density in the ED stack examined.

As an example of the application of the aforementioned sequence, Table XVI lists the main engineering parameters necessary to design or optimize ED stacks equipped with AMV and CMV electromembranes (Table II) and committed to the recovery of the sodium salts of some weak monocarboxylic acids of microbial origin (i.e., acetic, propionic, and lactic acid) and of a strong inorganic acid (i.e., chloride acid), as estimated by Fidaleo and Moresi (2005a,b, 2006).

As the salt molecular mass (M_B) increased from 58 to 112 Da, the transport number for Na^+ in the corresponding solution tended to increase from 0.4 to 0.6 for the progressively smaller equivalent conductance at infinite dilution (λ_0^-) of acetate, propionate, and lactate ions with respect to that of Cl^-. Nevertheless, the current within the electromembranes was almost exclusively carried by the counterions.

The effective solute (t_s) transport number, ranged from 93% to 98%, even if reduced to 88% for sodium lactate. The water transport number (t_W) increased from 9.3 to 15.6 and correspondently the maximum salt weight concentration in the concentrated stream ($C_{BC,max}$) ranged from 286 to 350 kg/m^3. Finally, while the surface resistance (r_c) of the cation-exchange membranes was found to be about constant ($5 \pm 2\ \Omega\ cm^2$), r_a tended to increase with M_B. However, the specific electric energy consumption (ε) slightly increased from 0.19 to 0.22 kWh/kg of salt recovered.

TABLE XVI

MAIN ENGINEERING PARAMETERS CHARACTERIZING THE ED RECOVERY OF NaCl, Na-A, Na-P, AND Na-L FROM MODEL SOLUTIONS[a,b]

Salt	M_B Da	t^+	t_s	t_w	r_c Ω cm^2	r_a Ω cm^2	t_c^+	t_a^-	ε kWh/kg	$C_{BC,max}$ kg/m^3
NaCl	58.4	0.40	0.969 ± 0.002	9.3 ± 0.1	6 ± 1	6 ± 1	0.97 ± 0.01	1.00 ± 0.01	0.19	338
Na-A	82.0	0.56	0.931 ± 0.003	14.8 ± 0.1	6 ± 2	12 ± 2	0.93 ± 0.01	1.00 ± 0.01	0.21	286
Na-P	96.1	0.59	0.982 ± 0.002	15.23 ± 0.04	2 ± 1	25 ± 3	0.95 ± 0.04	1.03 ± 0.03	0.20	344
Na-L	112.1	0.60	0.876 ± 0.002	15.60 ± 0.05	5.5	16.4	0.92 ± 0.01	0.96 ± 0.01	0.22	350

[a] As extracted from Fidaleo and Moresi (2004, 2005a,b, 2006).

[b] Effect of the salt molecular mass (M_B) on the cation transport number (t^+) in the corresponding solution; effective solute (t_s) and water (t_W) transport numbers; surface resistances (r_c, r_a) of, and counterion transport numbers (t_c^+, t_a^-) in cation- and anion-exchange membranes; specific electric energy consumption (ε) in the case of 90% salt recovery at 1 A, and maximum solute concentration theoretically achievable in the concentrating stream ($C_{BC,max}$).

Note: NaCl, sodium chloride; Na-A, acetate; Na-P, propionate; Na-L, lactate.

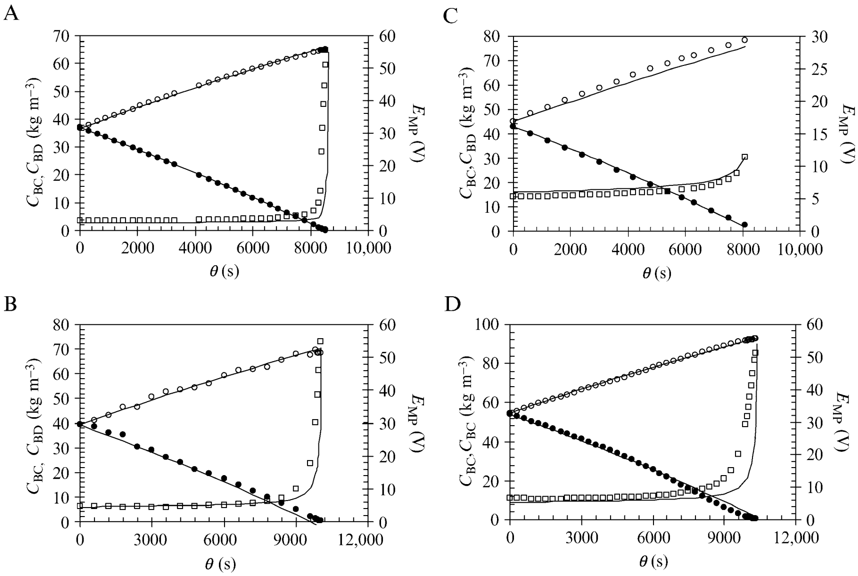


FIG. 22 Batch recovery of sodium chloride (A), acetate (B), propionate (C), and lactate (D) at 20°C, $v_s = 3$ cm/s, $I = 1$ A using 10 AMV and 9 CMV membranes (Table II): solute weight concentrations (C_{BC} and C_{BD}) in C (○) and D (●) tanks, and voltage (E_{MP}: □) applied to the membrane pack vs. time (θ). The continuous lines were calculated via Eqs 26, 27, and 18.

By integrating Eqs 28 and 29 and using Eq. 18 together with the independent parameters listed in Table XVI, it is possible to simulate the time course of the main variables involved in the batch electrodialytic recovery of the four sodium salts examined.

As an example, Figure 22 shows quite a satisfactory agreement between the experimental and calculated values of C_{BC}, C_{BD}, and E_{MP} against time (θ) for the laboratory-scale electrodialyzer used by Fidaleo and Moresi (2004, 2005a,b, 2006).

V. PRESENT PROBLEMS AND FUTURE PERSPECTIVES

Despite the ED industry has experienced a steady growth rate of about 15% since the late 15 years (Srikanth, 2004) and ED potentialities are numerous, its applications are still too marginally extended to the food industry. What are the reasons for such a scarce diffusion?

By tradition, the technical progress of the food industry has generally proceeded quite slowly with 20–30-year delay with respect to that of the chemical and pharmaceutical industries (Cantarelli, 1987). For instance, it is worth noting that falling film evaporators started to be used in the Italian citrus industry by the early 1970s in spite of the fact that they had been industrially manufactured in 1947 by *Majonnier Brothers Co*. on the behalf of *Florida Citrus Canners Cooperative* (Varsel, 1980) as a follow-up of the under vacuum concentration techniques developed during the World War II to concentrate highly thermosensitive materials, such as penicillin.

To counteract the typical misoneism of the world food industry, it is necessary to resort to appropriate scaling-up exercises in pilot- or industrial-plant scale to assess precisely the membrane process performance and reliability, as well as its economical feasibility. There are, however, a number of problems that have undoubtedly limited growth in ED membrane sales, like membrane-fouling problems, design considerations, cleanability, investment and membrane replacement costs, and competing technologies, such as NF and IER.

Membrane fouling and scaling are caused by soluble and insoluble impurities present in the feed such as insoluble salts, organic matter, colloidal substances, and microorganisms. Whereas the anionic membranes appear to be more liable to be fouled by organic matter, the cationic ones tend to be scaled by inorganic matter. To minimize such problems, as well as stack plugging, feed pretreatment via MF, UF, NF, or IER may be useful. Other approaches, such as the modification of the membrane properties (Grebenyuk *et al*., 1998) or use of pulsed electric fields (Lee *et al*., 2002b, 2003), appear to be expedient to alleviate anionic membrane fouling. In the great majority of cases, cationic membrane scaling was found to be almost reversible and kept under control by pH adjustment, EDTA, or citric acid addition. Thus, it is still lacking a well-defined procedure to moderate fouling and scaling in ED processing and there is a need for additional research on this issue so that the process can be optimized taking scaling and fouling into account.

The maximum cell voltage, which varies in the range of 0.8–1.5 V/cell under the current density recommended by the manufacturers, tends to increase with time as the charged groups in the electromembranes vanish with use as a result of their chemicophysical reactions with the feed contaminants. Beyond such potential difference limits, it is generally advisable to replace the membranes to limit the overall electric power consumption.

ED membranes can be generally cleaned with dilute acidic and alkaline solutions, as well as enzyme solutions.

When chemical cleaning is inefficient, current reversal is the method of choice.

In the case of clarified feeds and low current densities, membrane lifetime can be as long as seven or 10 years for brackish water desalination or drinking water nitrate removal, respectively. However, if the feed solution is fouling or scaling or the ED separation plant has not been well designed or is not properly conducted, membrane lifetime is no longer than a year.

The incomplete comprehension of mass transfer mechanisms in ED membrane systems is in all probability responsible for the difficult design of industrial plants and for their limited diffusion. For instance, in the food biotechnology sector ED applications are still in their infancy since quite a limited number of the novel processes studied so far in laboratory- and pilot-scales and reviewed here have been converted into industrial realities yet, except for the recovery of the sodium salt of unspecified organic acid from clarified fermentation broths, as well as amino and organic acids (Gillery *et al.*, 2002).

This unequivocally means that ED-processing potentialities have not been completely exploited and much more is needed to account for all the key parameters (i.e., current density, cell voltage, current efficiency, solute concentration in the diluting and concentrating streams) optimizing ED performance.

The electric potential difference is the driving force of the ED process since it determines the flux of ions across the membranes, which corresponds to a current density. The greater the current density, the smaller the membrane surface area required becomes. This minimizes the investment and maintenance costs, but boosts the electric power consumption per kg of solute recovered. Moreover, by increasing j the faster ion transfer through the membranes enhances the polarization concentration effects at the boundary layers. As soon as the solute concentration at the membrane surface is zero, the limiting current density (j_{lim}) is achieved. Since the Donnan potential difference (E_{D}) in any cell pair tends to infinite, this would result in quite a great increase in cell voltage. As j exceeds j_{lim}, the pH of the dilute or concentrate falls or increases, respectively, and Ω reduces. Even if it is recommended to keep j smaller than 70–80% of j_{lim}, for any given application it is essential to assess the effect of solute concentration and feed superficial velocity on this critical parameter by performing a series of current–voltage tests.

To maximize the overall current efficiency, all the parasitic phenomena occurring in the ED stack are to be minimized by getting rid of imperfect gaskets and membranes with pinholes leading to liquid leakage and dripping. Also the manifolds are to be made of nonconductive materials to limit shunt or stray currents running in the nonactive cell area. Thus, an optimal stack design feature is needed together with low values of cell voltage and ratio of conductivity in the concentrate and dilute loops. However, in the case of very soluble solutes, this ratio can be as high as 20, a much higher value than that achieved in RO units, which explains why ED is used to produce table salt from seawater in Korea and Japan. The minimum solute concentration in the diluting stream is generally associated to an electric conductivity (χ) of about 0.05 S/m to limit the ohmic resistance of the diluting compartments.

The maximum temperature in the ED stacks used for the food industry was generally 35–40 °C, but novel anionic membranes are claimed to allow operation up to 60 °C, this being useful for viscous and low-χ products such as sugar syrups or molasses.

Despite many of the ED membrane applications might be regarded as mature, being established in the 1970s, they are still relatively new owing to the fact that no membrane-based process is today an established procedure for given production processes. This is true even in the case of brackish- and sea-water desalination, the ED technology being competed by MSFD and RO depending on the TDS content of brackish or sea water and plant capacity (Table VII).

Moreover, the economics of such a separation technique is *a priori* expected to be controlled by electric energy costs, but this is not always true and should be verified case by case. For instance, when dealing with the batch electrodialytic recovery of trisodium citrate at pH 7, disodium itaconate at pH 6, or sodium lactate at pH 5 from aqueous solutions, it was found that, in the optimal operating conditions, the contribution of depreciation and general plant maintenance and annual membrane replacement ranged from 60% to 66% of the overall operating costs per unit mass of solute recovered, that of electric energy was about one third for citrate and itaconate recovery, and just 20% for lactate recovery while the remaining 8–14% was pertaining to labor costs (Moresi and Sappino, 2000). In this way, it was first shown that sodium lactate ED recovery was by far much less expensive than that of trisodium citrate or disodium itaconate. Second, it was possible to evaluate how any enhancement in ion mobility through the ED membranes or extension in their service life would have minimized the overall membrane surface area to be installed and thus reduced plant investment and maintenance costs. Third, the ED recovery of these sodium salts was mainly controlled by the so-called investment-related operating costs rather than the electric energy costs.

So, any attempt to minimize the specific electromembrane costs, especially now that the membrane market is open to new Far East manufacturers (Table II), is expected to reduce significantly the investment and membrane replacement costs.

This will be a prerequisite for promoting, in the short-medium term period, further interest toward ED since it might avoid the great pollution problems caused by the disposal of the enormous amounts of calcium sulfate produced by the traditional citrate or lactate recovery process most largely used in the industrial scale or simplify the complex operations actually used to purify for instance itaconic acid crystals.

In conclusion, a greater knowledge of the effect of the key controlling parameters of this powerful separation technique, as well as improvement in membrane life time of the currently available commercial electromembranes and reduction in their costs, would ensure further growth beyond desalination and salt production and foster ED applications in the food sector, as well as in the chemical, pharmaceutical, and municipal effluent treatment areas. This will of course need extensive R&D studies and will highly likely result in hybrid processes combining ED to other separation techniques, such as NF, IE, and so on, so as to shorten present downstream and refining procedures.

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