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Design and Performance of an Economical Brine Electrodialysis Process

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ABSTRACT

The first commercial-scale salt production by the ion-exchange process was begun in 1961 at Shin-Nihon Chemical Industry Company's Onahama Plant. Long-term membrane and process stability was fully established in the mid-1960s and the development effort since then has centered largely on reducing the salt production cost by reducing the electrical consumption in the membrane stack of the electrodialyzer.

One major advance resulting from this effort has been the reduction of ohmic loss across the membrane stack, especially across its seawater compartments, by adopting an "alternating thickness" spacer and gasket configuration in which 0.75 mm-thick gaskets and 0.5 mm-thick spacers are used to obtain a compartment thickness of only 0.5 mm. The reverse configuration is utilized in the brine cells, with 0.75 mm-thick spacers and 0.5 mm-thick gaskets, to maintain cell and stack alignment.

A second major advance has been the development of the HM-II and HM-III type ion-exchange membranes, which are characterized by reduced ohmic loss across the membrane in large-scale salt plants with no adverse effect on the other membrane properties such as durability or osmotic concentration.

With the low power consumption of the HM-II and HM-III systems incorporating these advances, the proportional cost of salt production has been reduced to about one-third of the total production cost. The main target of the cost reduction effort has therefore now shifted to reducing fixed costs. The salt production capacity of an electrodialyzer is proportional to its total electric current. Investigation is therefore now in progress to increase the limiting current density of the membrane stack, thereby obtaining a higher salt yield per electrodialyzer, and thus reducing the fixed cost. The "alternating thickness" configuration with the HM-II membrane system provides an effective basis for adoption of high current density operation and reduced fixed costs.

INTRODUCTION

In 1951, Asahi Chemical began organized research directed towards the development of an ion-exchange membrane process for brine production from seawater. Several years of intensive work by the research team led to the selection of a three-dimensionally crosslinked copolymer of styrene and divinylbenzene as the basis of stable cation- and anion-exchange membranes, and to the development in 1958 of fully operational large-area membranes, more than 1 m^2.

DEVELOPMENT OF FILTER-PRESS TYPE ELECTRODIALYZER

The large-area membranes were utilized in the development and design of a prototype electrodialyzer containing rubber gaskets and spacers to maintain a uniform distance and seal between adjacent membranes. This work led to the development of the filter-press type electrodialyzer, essentially comprised of anode, cathode, and 6–8 membrane stacks each containing some 300 pairs of anion- and cation-exchange membranes separated by an equal number of gaskets and spacers. Research and development at two other Japanese chemical manufacturers, Tokuyama Soda Co. and Asahi Glass Co., have also led to their adopting filter-press type electrodialyzers for brine production utilizing ion-exchange membranes.

EARLY DESIGN AND OPERATION OF SALT PRODUCTION PLANTS

The first full-scale salt production plant to employ the ion-exchange process, utilizing a number of large-scale electrodialyzers, was designed and constructed in 1961 by Asahi Chemical at the Onahama plant site of Shin-Nihon Chemical Industry Co. The

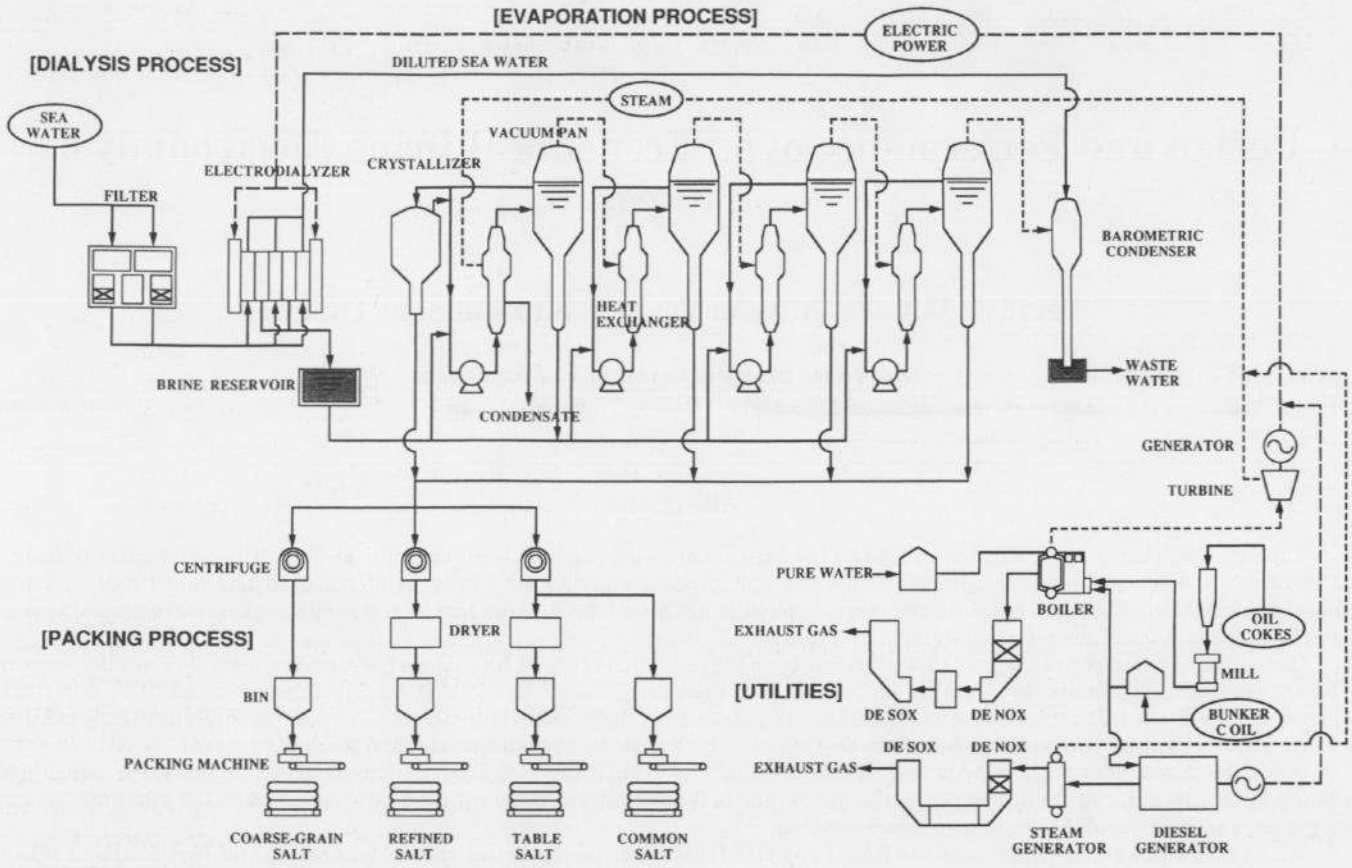

Fig. 1. Flow sheet of ion-exchange membrane process.

plant encountered difficulties in maintaining stable continuous production, due to physical degradation of the membranes caused by calcium carbonate and calcium sulfate precipitates on and inside the membranes. This problem was finally resolved in 1964 by the invention of new membranes with monovalent ion selectivity — a cation-exchange membrane with permselectivity for sodium and potassium ions rather than divalent cations, and an anion-exchange membrane with permselectivity for chloride ion rather than divalent anions.

The basic economic viability of the process was established by the monovalent-ion permselective membranes and the large-scale, energy-efficient electrodialyzers, and solar salt producers in Japan began tentative adoption of the process, by partial conversion of their salt production capacity. Akoh Sea Water Salt Co. and Naruto Salt Co. introduced test plants of 10,000 t NaCl annual capacity in 1965 and 1966, respectively, designed and equipped by Asahi Chemical. The stable, economical performance of these plants led to a decision by the Japan Monopoly Corporation for the conversion of all existing Japanese solar salt production capacity to the ion-exchange process in 1972. Seven large-scale salt production plants, each of about 150,000 t NaCl annual capacity, were constructed at various locations, most of which utilized the existing landholdings and manpower of the solar salt producers' cooperative organization.

PROCESS IMPROVEMENTS

The development effort since 1965 has centered primarily on improving the membrane and electrodialyzer performance, to reduce the power consumption and thus the salt production cost.

The overall production process consists of many electrodialyzers, to obtain concentrated brine from seawater, and one multi-effect evaporator train, where the product brine is evaporated to obtain crystalline salt. The process is shown schematically, in its present mode, in Fig. 1. The key factors for reducing energy consumption, and thus production cost, have been a reduction of the unit power consumption of the electrodialyzer, an increase in product brine concentration, and a high steam economy in the multi-effect vacuum evaporators.

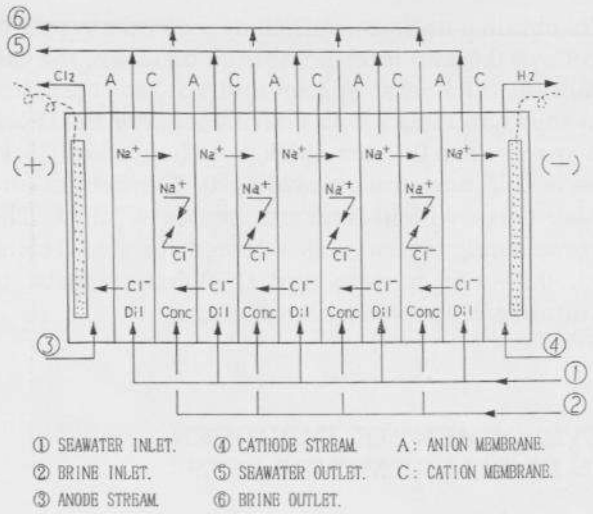

Fig. 2. Schematic diagram of electrodialyzer function yielding brine from seawater.

TABLE 1

Potential drop across components of electrodialyzer

Membrane	HM-II	HM-III
Unit power consumption[a]	170 kWh/t salt	150 kWh/t salt
Potential drop per pair of D- and C-cells	0.193 volt	0.182 volt
Breakdown of potential drop[b]		
Anion membrane	0.055 volt	0.051 volt
Cation membrane	0.067	0.060
D-cell compartment	0.061	0.061
C-cell compartment	0.010	0.010

[a]At 25°C and 3 A/dm^2, 0.4 eq/l at D-cell outlet.
[b]Concentration potential (E_o) across D-cell/C-cell pair: 0.088 volt.

The main gains in the past twenty years have been related to electrodialyzer and membrane performance, permitting the production of more highly concentrated brine at a lower electric potential between anode and cathode and an increase in unit production capacity, or product brine capacity per membrane pair.

UNIT POWER CONSUMPTION OF ELECTRODIALYZER

The basic function of the electrodialyzer resulting in the production of brine from seawater is shown schematically in Fig. 2. The overall electric potential through one electrodialyzer consists of the sum of the electric potentials across its membranes, the ohmic losses of its seawater and brine compartments, and the electrolysis potentials of hydrogen and chlorine gas generation at its two electrodes. Typical electric potentials across the electrodialyzer components are shown in Table 1. In a typical electrodialyzer, as illustrated in Fig. 3, there are 2,400 pairs of seawater and brine cells (D- and C-cell, respectively), formed by essentially the same number of cation- and anion-membrane pairs together with their rubber gaskets and spacers. Each cell consists of a seawater or a brine compartment, with the cell "walls" formed by one cation membrane and one anion membrane. The electric potential across each pair of sea-

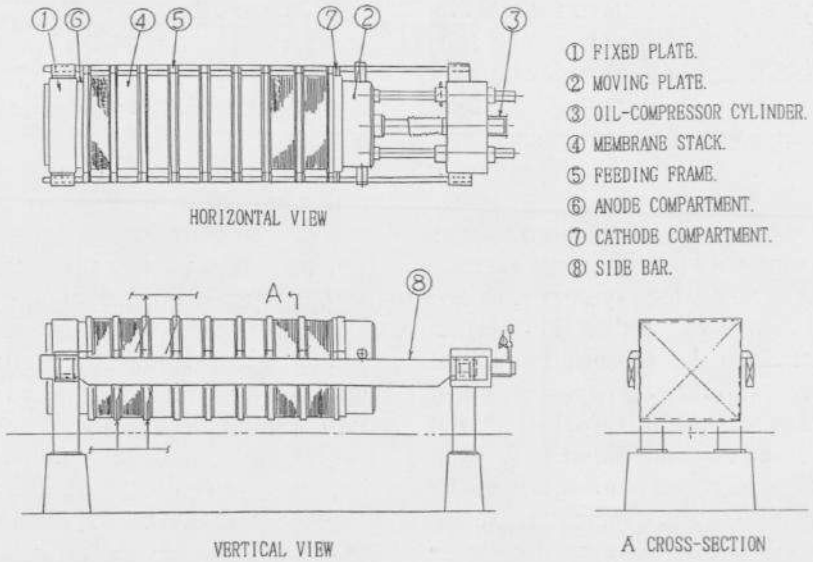

Fig. 3. Filter-press type electrodialyzer.

water and brine cells largely determines the overall electric potential through the electrodialyzer. The electric potential of the D-cell compartment holds a larger role than that of the C-cell compartment in reduction of the unit power consumption of the electrodialyzer, because the electric resistance of seawater is more than five times higher than that of the brine stream in the C-cell.

The ohmic loss across the D-cell compartments has been reduced by the development of two-step electrodialysis, to increase the seawater concentration, and by reducing the intermembrane distance in the D-cell. In the early electrodialyzers the distance was 1 mm. It was subsequently reduced to 0.75 mm and has now been further reduced to 0.5 mm. The main obstacle to this reduction was the difficulty of maintaining uniform and sufficient seawater feed to all 300 to 400 D-cells in the stack. With non-uniform flow distribution, the seawater concentration near the outlet of any D-cell subjected to a low seawater feed rate will tend to decrease, leading to serious membrane polarization within the D-cells where the seawater concentration falls below a certain limit.

Membrane polarization occurs on the surface of the membrane, in regions where the water molecule is decomposed to hydrogen and hydroxide ions due to a steep potential gradient across the boundary layer adjacent to the membrane. It may result in the formation of magnesium hydroxide or calcium hydroxide precipitates on and inside the membrane, and thus in serious membrane degradation.

To obtain a uniform, sufficient seawater supply to D-cells of 0.5 mm intermembrane distance, the "alternating thickness" spacer and gasket configuration shown in Figure 4 was developed. For the D-cell the spacers are 0.5 mm thick but the gasket thickness is 0.75 mm, thus providing 0.75 mm inlet and outlet ports which facilitate seawater flow. The reverse configuration was adopted for the C-cells, with 0.75-mm spacers and 0.50-mm gaskets, to maintain cell and stack alignment.

DEVELOPMENT OF IMPROVED ION-EXCHANGE MEMBRANES

The electric resistance of an ion-exchange membrane is generally much higher than that of the liquids in the electrodialyzer, and is therefore an important factor in reducing the electrodialytic power consumption. As shown in Table 1, the ion-exchange membranes account for more than 60% of the total electric potential drop across a cell pair.

It is generally very difficult to reduce the electric resistance of an ion-exchange membrane without adversely affecting its mechanical strength, durability, and osmotic concentrations. As shown in Table 2, however, these membrane characteristics have been substantially improved, through studies on the base polymers and the chemical and physical structure of the membranes.

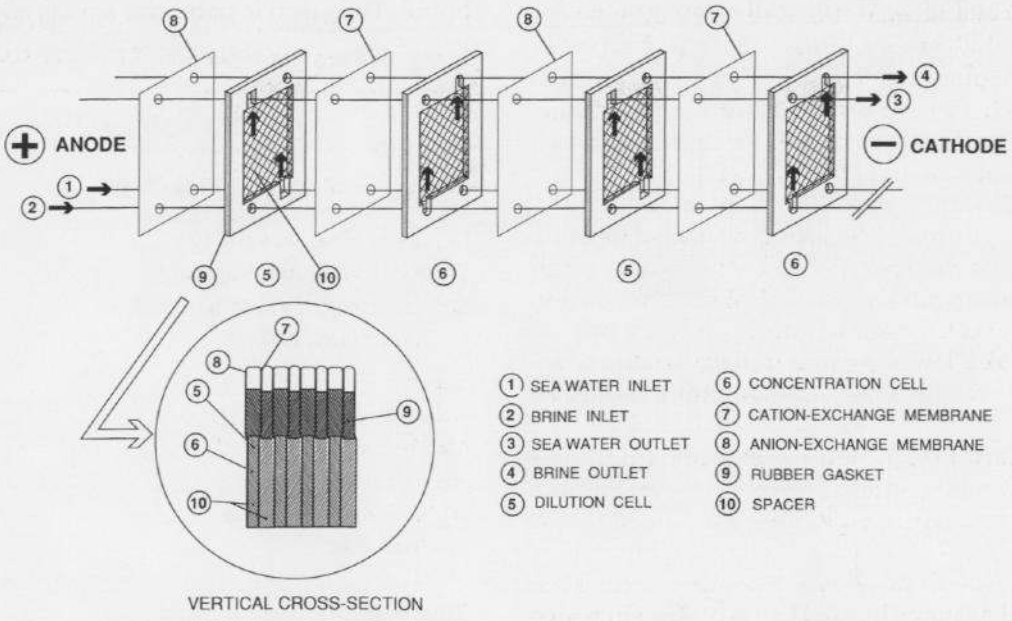

Fig. 4. Schematic structure of membrane stack and alternating thickness cell configuration.

TABLE 2

Improvement of membrane properties for electrodialysis process (Seko et al., 1983; Miyauchi and Omura, 1984; Shiroki et al., 1991)

Year[a]	Asahi membranes		Main improvements
	(Cation)	(Anion)	
1961	CK-1	CA-1	Styrene-divinylbenzene copolymer, homogeneous; 1300×1300 mm
1965	CK-2	CA-3	High selectivity for monovalent ions
1971	K-102	A-102	Fibre-reinforced, heterogeneous-type; 1300×1300 mm
1981	K-162	A-162	Low electric resistance; HM-I type
1982	K-172	A-172	Low electric resistance; 170 kWh/t salt at 25°C and 3.5 A/dm^2; HM-II type
1985	K-182	A-182	Low electric resistance; 150 kWh/t salt at 25°C and 3.0 A/dm^2; HM-III type

[a]Year of initial commercial utilization.

PERFORMANCE CHARACTERISTICS OF RECENT ELECTRODIALYZERS

Constant research and development in the years since 1965 have brought substantial advances in both ion-exchange membranes and electrodialyzer design, as shown in Table 3 by unit power consumption and other operational characteristics of the most recent electrodialyzer systems, utilizing the HM-II and HM-III membranes. The HM-II system, containing 2485 HM-II membrane pairs with an intermembrane distance of 0.75 mm in the D-cells, achieved an energy efficiency of 185 kWh/t NaCl at a current density of 3.5 A/dm^2, with a production capacity of 16,000 t NaCl per year. The unit power consumption has been further reduced, to 150 kWh/t NaCl, by the HM-III system utilizing 2400 HM-III membrane pairs with a D-cell intermembrane distance of 0.50 mm, though at a lower current density and production capacity, of 3.0 A/dm^2 and 14,000 t NaCl per year.

The standard design parameters and rated performance for an large-scale ion-exchange membrane plant, based on current operations, are given in Tables 3, 4 and 5.

The very low unit power consumption of the HM-II and HM-III systems has led to a situation in which further reductions in overall production cost will be made largely in the area of fixed cost, rather than

TABLE 3

Standard operating conditions of electrodialyzer

Membrane type	HM-II	HM-III
Electrodialyzer		
Membrane area (dm^2)	140	140
Effective area (%)	82.8	82.8
Cell pairs (no.)	2485	2400
D-cell thickness (mm)	0.75	0.5
Operating conditions		
Total DC current (A)	490	420
Current density (A/dm^2)	3.5	3.0
Total seawater flow-rate (m^3/h)	420	216
Seawater concentration		
Inlet (NaCl eq/l)	0.53	0.53
Outlet (NaCl eq/l)	0.43	0.39
Rated performance		
Brine concentration (NaCl g/l)	200	200
Unit power consumption (kWh/t salt)	185	150
Production capacity (t/year)	16000	14000

TABLE 4

Design base for a large-scale (250,000 t/year) salt production plant

Number of electrodialyzers	17
Number of cell pairs	42,245 pairs
Seawater feed	30.84 million t/year
Brine production	1.46 million t/year
Power consumption for ED	48,530 MWh/year
Power consumption other than ED	20,630 MWh/year

TABLE 5

Breakdown of salt production cost

DC power for electrodialyzer[a]	14%
Steam for vacuum evaporator[b]	16
Seawater feed, chemicals	5
Proportional cost	35
Labor	11
Utilities	6
Membrane replacement[c]	2
Amortization	29
Maintenance, materials	17
Fixed cost	65
Total cost	100

[a]At 5.6 ¢/kWh; [b]At 8.8 ¢/t; [c]Membrane attrition, 2%/year.

proportional cost. As shown in Fig. 5, the energy and other proportional costs with these two systems, as estimated on the basis of operation at 3.0 and 3.5 A/dm^2 current density with a large-volume facility, now comprise only about 35% of the total production cost, while the labor, depreciation and other fixed costs represent about 65%.

As also indicated by Fig. 5, an important means of lowering this fixed cost will be the achievement of higher current density without significantly increasing the unit power consumption of the electrodialyzer, since a higher current density results in a larger production capacity with a given size and number of electrodialyzers.

The maximum permissible current which may be used in the electrodialyzer is determined largely by the limiting current density, which is a function of the mobility of ions through the membrane. More specifically, it is determined by the ion flux of sodium and chloride ions migrating across the boundary layer between the bulk seawater and the membrane surface due to both the concentration differential and the electric potential. The limiting ion flux, and thus the limiting current density, can be expressed as follows.

$$I_{LiM} = \frac{F}{\delta} \cdot \sum_{i} \frac{Di \cdot Ci}{\bar{\tau}_i - \tau_i}$$

where F is the Faraday Constant, δ is the thickness of boundary layer, Di is the diffusion constant of ion i, Ci is the bulk concentration of ion i, $\bar{\tau}_i$ is the transport number of ion i through membrane, and τ_i is the transport number of ion i in the boundary layer.

As indicated by this equation, the limiting current density is affected by engineering parameters related to the bulk ion concentration and the boundary layer thickness, and cell and electrolyzer design has therefore included criteria such as the maintenance of turbulent seawater flow at the membrane surface as well as uniform flow distribution to the D-cells of the membrane stack.

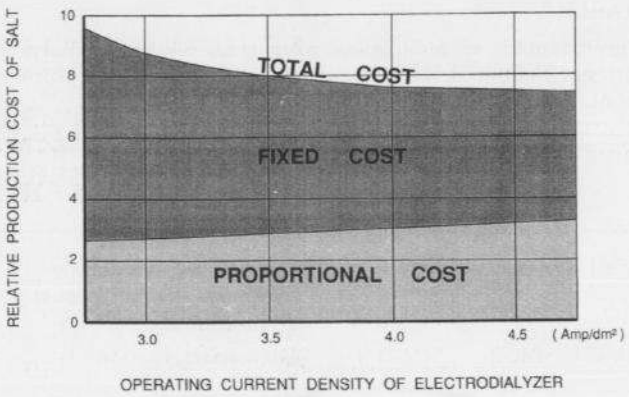

Fig. 5. Production cost vs. current density of electrodialyzer.

In practice, precise determination of the limiting current density is virtually impossible, because of the difficulty of detecting the slight change in electric potential across the membrane which occurs at the onset of membrane polarization. A limiting current density of about 4.5 A/dm^2 has been obtained in a test electrodialyzer of the HM-II type containing 50 D-cells in the alternating thickness configuration, and we estimate that the ultimate electrochemical limit of the current density may be some 20%–30% higher. Development work to increase the current density in large-volume electrodialyzer operations to 4.5 A/dm^2 and perhaps higher, and thus reduce the fixed cost for the salt production process, will of necessity center on increasing the uniformity of both the seawater flow into the D-cell and the ion flux near its membrane surface.

REFERENCES

Miyauchi, H. and Omura, J., 1984. Denkitoseki, Shokuendenkai to Kinouseimaku. In: MOL, 3: 57–64.

Seko, M., Miyauchi, H. and Omura, J., 1983. Ion Exchange Membrane Applications for Electrodialysis, Electro-reduction and Electrohydrodimerization. In: Proceedings of Ion Exchange Membrane Symposium, London.

Shiroki, H., Hiyoshi, T., and Ohta, T., 1991. Recent Development and Operation Dynamics of New Ion Exchange Membrane Series Aciplex-F from Asahi Chemical. In: Proceedings of London International Chlorine Symposium.