Energy Savings in Salt Manufacture by Ion Exchange Membrane Electrodialysis

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ABSTRACT

Although salt has been manufactured successfully for many years at plants in Japan, the Republic of China and the Republic of Korea by electrodialysis utilizing ion exchange membranes, rising oil prices since 1973 have increased the proportion of energy cost to over 50% of the total salt manufacturing cost at these plants. It has therefore become increasingly important to find ways to reduce the consumption of the electric and the thermal energy used in these plants, and important improvements have been developed and implemented. This paper describes current and scheduled improvements for energy savings in the ion exchange membranes, electrodialyzer, and evaporating crystallizer.

INTRODUCTION

Basic Methods of Table Salt Manufacture

Table salt has traditionally been obtained by mining or by solar evaporation. Where large salt deposits are accessible, as in Europe and America, rock salt is mined and refined. Where there is a constant supply of sunlight, as in Mexico, Australia and China, seawater is evaporated by solar heat in salt fields.

In the monsoon regions of Southeast Asia and Japan, with no salt deposits and frequent rain, it has always been difficult or impossible to produce salt in any quantity by these methods.

The Ion Exchange Membrane Process

This problem has been solved in recent years by development of the ion-exchange membrane process, in which crystalline table salt is obtained from seawater by selective concentration with electric energy, followed by evaporation and crystallization by heat. This process is unaffected by the weather and has made possible the stable production of table salt in these areas.

The process was first introduced in 1961 in Japan, and all table salt production in Japan has been converted to this process by 1972. The technology has also been exported to the Republic of China and the Republic of Korea by Asahi Chemical for production of a stable supply of table salt, as shown in Table 1.

The ion-exchange membrane process consists of two basic steps as shown in the block diagram of Figure 1. The first step is electrodialysis by ion-exchange membrane, to selectively obtain a concentrated brine from seawater. The second involves the extraction of salt crystals from this brine, by multi-effect evaporation and crystallization. The required energy is provided by electricity in the first step, and by heat in the second.

Energy Consumption in the Ion-Exchange Membrane Process

Although the electric and thermal energy can be obtained separately, with one purchased from an electric

TABLE 1

Salt Manufacturing Plants Using Electrodialysis in the World

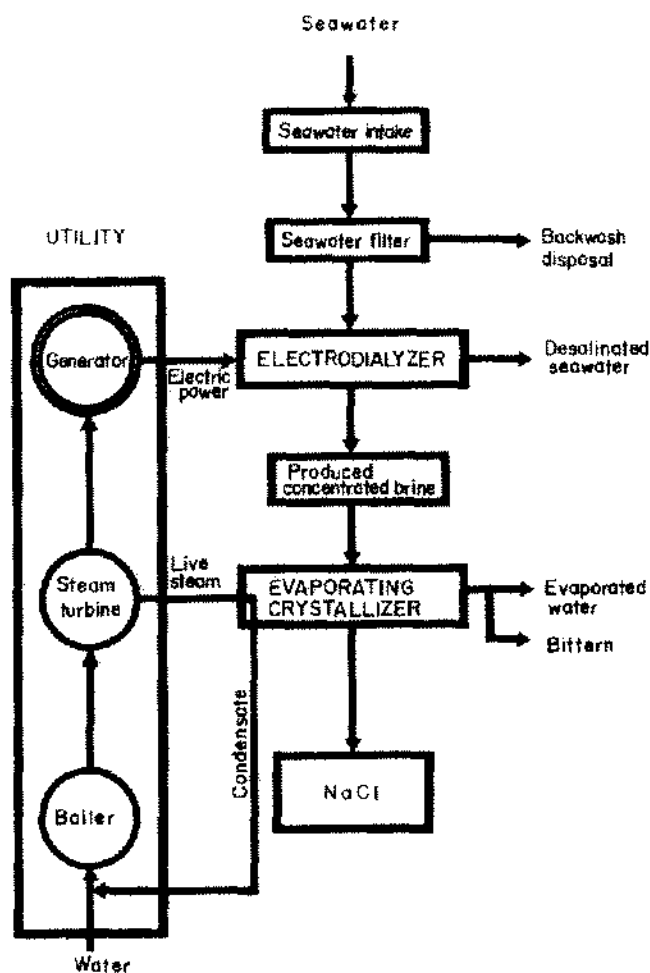| Name of the Company	Production Capacity (MT-Salt/Y)	Technology	Location
Shin Nihon Chemical Ind. Co.	186,000	Asahi Chemical	Japan
Ako Sea Water Chemical Ind. Co.	175,000	Asahi Chemical	Japan
Naruto Salt Mfg. Co.	184,300	Asahi Chemical	Japan
Naikai Salt Works	192,000	Asahi Glass	Japan
Sakito Salt Works	179,000	Asahi Glass	Japan
Kinkai Salt Mfg. Co.	173,000	Tokuyama Soda	Japan
Sanuki Salt Mfg. Co.	172,700	Tokuyama Soda	Japan
Tung-Hsiao Electrodialysis Salt Factory	110,000	Asahi Chemical	Taiwan
Hanju Corporation	150,000	Asahi Chemical	Korea
Total	1,522,000	—	—

Seawater

Figure 1. Flow sheet of salt manufacturing plant.

is therefore necessary to separate about 35.7 tons of water and 0.3 ton of other salts. To achieve this separation simply by thermal evaporation would require about 22,000,000 kcal per ton of NaCl, which is equivalent to about 2,400 liters of heavy oil. This would be prohibitively expensive, unless the thermal energy is practically free, as in the solar evaporation salt field. With electrodialysis, however, the energy requirements for this separation can be reduced to practical levels.

The basic principles of electrodialysis with ion-exchange membranes are illustrated in Figure 2. A series of alternating anion- and cation-exchange membranes is placed between two electrodes and subjected to a direct current flow. The desired salt components pass selectively through the respective membranes to form a concentrated brine, which is then fed to an evaporating crystallizer to obtain the product salt crystals. The properties of the membrane must allow it to fulfill the three basic functions of (1) selectively extracting table salt from seawater and excluding other salts, (2) reducing the energy requirements for this extraction to the lowest possible level, and (3) concentrating the brine to the greatest possible degree.

Some of the properties required for these functions are mutually contradictory and thus make technical development difficult. One obvious conflict is between the desirability for high brine concentration and low electric power consumption. Lower levels of electric energy tend to result in lower brine concentration, which in turn leads to greater consumption of thermal energy for evaporation and crystallization. The membrane must be carefully designed to provide the optimum balance between electrical and thermal energy requirements, and thus minimize the total energy costs. Further, the optimum membrane properties will vary with the relative energy prices prevailing at the particular plant.

Potential Areas of Energy Cost Reduction

The total energy cost can be reduced in two basic ways:

1. Reducing energy consumption
   a. In the electrodialysis process
   b. In the evaporating crystallization process
2. Reducing the price of the energy source
   a. By conversion to a cheaper fuel, such as from heavy oil to coal
   b. By coordinated operation of a large power plant and the salt manufacturing plant.

This report deals mainly with the reduction of energy consumption in the electrodialysis process and the optimum balance between energy forms in a plant equipped with dedicated power generation facilities. It also indicates the advantages and desirable membrane performance for operation in conjunction with large power plants.
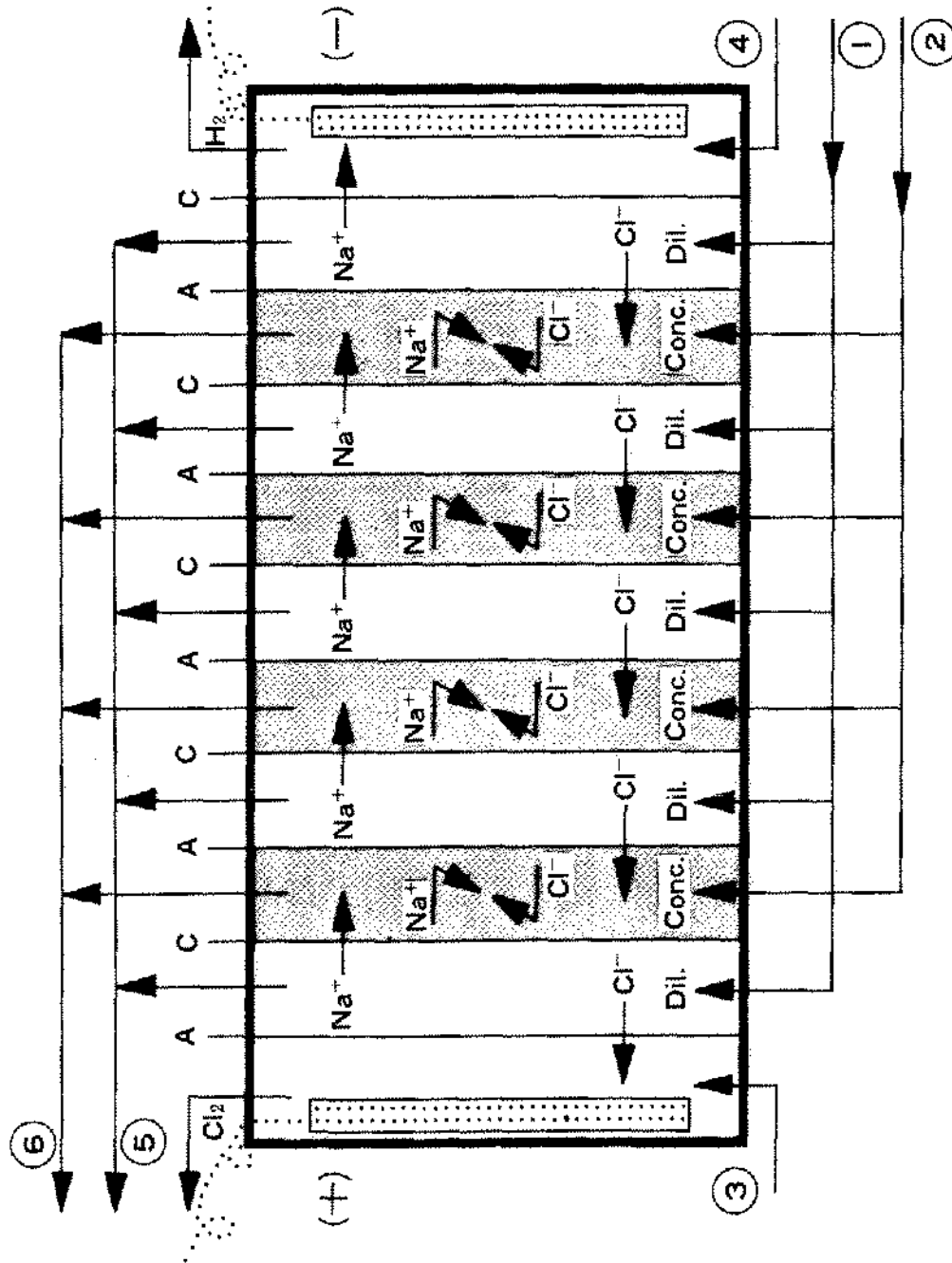
power company and the other obtained by burning heavy oil, this does not allow full utilization of the energy contained in the heavy oil. Therefore, dedicated power generating facilities are installed at most of the plants, to meet both the electricity and the steam requirements, while fully using the latent energy of the heavy oil. Because low-pressure steam is sufficient for evaporation and crystallization, the back-pressure steam of the turbine generator also can be used.

Even with this highly efficient utilization of the heavy oil, the sharp rises in oil and electricity prices since 1973 have tended to increase the proportion of energy costs to about 50% or more of the overall production cost, and they also have made further reduction in energy consumption highly desirable. For this purpose, it is necessary to consider the basic relation between the electric and thermal energy requirements of the ion-exchange membrane process.

One ton of seawater contains about 27 kg of table salt, about 8 kg of other salts such as magnesium chloride, and about 965 kg of water. To produce one ton of table salt, it

Figure 2. Principle of electrodialysis.

1, Inlet of dilution stream. 2, Inlet of concentration stream.
3, Anode compartment stream. 4, Cathode compartment stream. 5, Outlet of dilution stream.
6, Outlet of concentration stream.

Methods of Reducing Energy Consumption

The total energy consumption is a combination of the electric power consumption for selective concentration of seawater, thermal energy consumption for evaporation and crystallization of the concentrated brine thus obtained, and auxilliary electric power consumption for plant operation.

Energy consumption in electrodialysis. The unit consumption on electric power in electrodialysis (E), which is the main electric energy requirement of the overall salt manufacturing process, can be expressed by the following equations:

$$S = \frac{3,600\,(sec) \times 58.45\,(mol.wgt) \times 10^{-6}}{96,500\,(coul)} \times Iop \times \eta$$

$$P = V \times Iop \times 10^{-3}$$

Therefore:

$$E = P/S = \frac{V \times Iop \times 10^{-3}}{\dfrac{3,600 \times 58.45 \times 10^{-6}}{96,500} \times Iop \times \eta}$$

$$= 458.6 \times \frac{V}{\eta}$$

Also:

$$V = Em + Iop \times (Rd + Rc + Rm + Ro)$$

Therefore:

$$E = 458.6 \times \frac{Em + Iop \times (Rd + Rc + Rm + Ro)}{\eta}.$$

In these equations,

S　=　Amount of salt produced ($T-NaCl/h.m^2.cell$)
P　=　Electric power for electrodialysis ($kW/m^2.cell$)
E　=　Unit consumption of electric power for electrodialysis ($kWh/T-NaCl$)
V　=　Cell voltage (volt/cell)
Em　=　Membrane potential (volt/cell)
Iop　=　Operating current density (A/m^2)
η　=　Overall efficiency (production of current efficiency, purity of table salt in brine, rectifier efficiency, and efficiency of salt crystal extraction from brine)

and Rd, Rc, Rm, and Ro are, respectively, the electric resistances of the dilution compartment, concentration compartment, ion-exchange membranes and other parts, in $\Omega m^2/cell$.

The unit consumption of electric power for electrodialysis (E) is, therefore, largely dependent on the performance of the ion-exchange membrane and in particular on its electric resistance, current efficiency and selective permeability to table salt, which also affects the brine purity. Although (E) can be reduced by lowering the operating cur-

rent density (Iop), this also lowers the amount of table salt produced (S), and both factors must therefore be considered in determining the optimum Iop.

Figure 3 indicates the variation in the unit power consumption for electrodialysis with cell resistance (R = Rd + Rc + Rm + Ro) and overall efficiency (η), at Iop = 3.5 A/dm^2 and Em = 0.09 volt/cell.

Thermal Energy for Evaporation and Crystallization. In the evaporating crystallizer, the concentrated brine from the electrodialysis process is heated to the vaporization temperature. As the water evaporates, the salt crystals are formed and recovered. Figure 4 shows the relation of the incoming brine concentration and the thermal energy required to recover crystalline NaCl.

Incorporation of Dedicated Power Plant. In most table salt plants, the overall consumption of electric and thermal energy has been significantly reduced by incorporation of a dedicated power plant which provides both electricity and low-pressure steam, as shown in Figure 5.

Table 2 shows the relation between the concentration of brine obtained by electrodialysis and the fuel consumption levels with triple-, quadruple-, quintuple-effect evaporating crystallizers, and the maximum power generating capacities for each case. The following data were used for these calculations:

Heavy oil	9,200 kcal/l
Boiler efficiency	92%
Steam from boiler	70 atm., 480°C
Power generating efficiency	92%

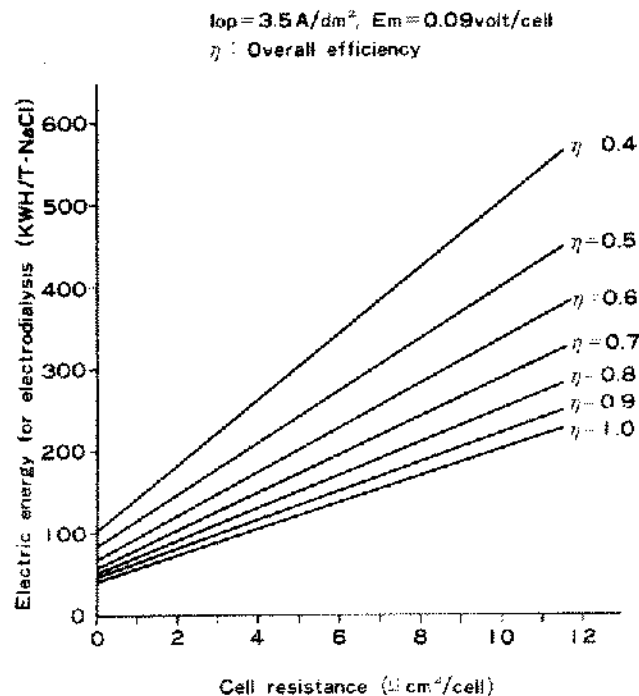Iop = 3.5 A/dm², Em = 0.09 volt/cell
η : Overall efficiency

Figure 3. Relation of electric energy, cell resistance and efficiency.
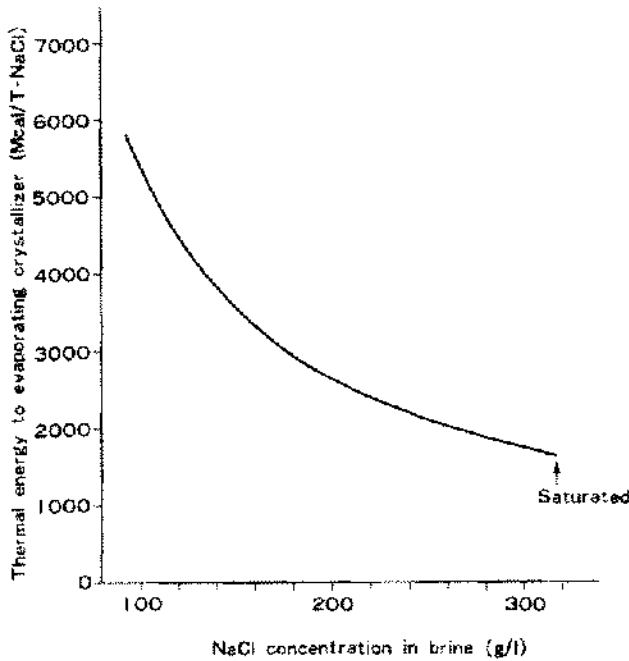
Figure 4. Relation of thermal energy and NaCl concentration.

Figure 5. Flow sheet of boiler, evaporating crystallizer and turbine generator.

Temp. of saturated steam supplied to the first evaporating crystallizer

3-effect	100°C
4-effect	120°C
5-effect	140°C

Steam economy

3-effect	2.64
4-effect	3.40
5-effect	4.08.

Figures 6, 7, 8 and 9 indicate the energy costs for salt manufacturing by the ion-exchange membrane process
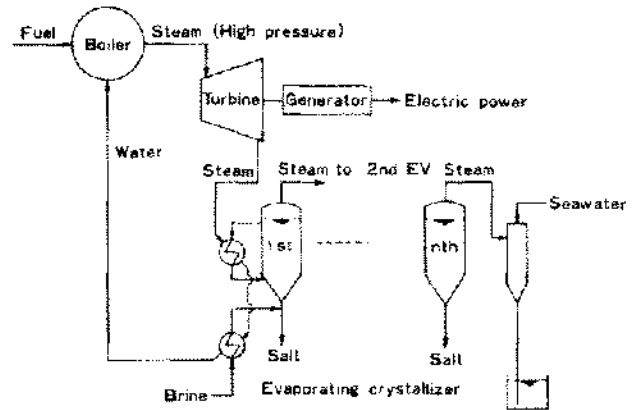
with a dedicated power plant, as related to the power consumption for electrodialysis and the NaCl concentration in the brine obtained by electrodialysis. In each figure, the single circle indicates the electrodialytic performance in 1979, and the double circle indicates the present electrodialytic performance.

The effect of improved electrodialytic performance on the overall energy cost varies with the fuel price, the electric power price, and the type of evaporating crystallizer. With a triple-effect evaporating crystallizer and the energy prices shown in Figure 6, the improved electrodialytic performance results in a saving of about 2,200 Yen/T−NaCl. As shown in Figure 8, the overall energy cost can be further reduced by about 2,800 Yen/T−NaCl to less than 6,000 Yen/T−NaCl, by conversion from heavy oil to coal.

The direction to be pursued in research and development for improved electrodialytic performance is thus closely related to the energy prices and the type of evaporating crystallizer. If the price of electric power is high in

TABLE 2

Relation Between the Concentration of Brine, the Heavy Oil Consumption and the
Maximum Power Generating Capacity

NaCl Concentration in Brine (g/l)	Heavy Oil Consumption (1/T−NaCl)			Maximum Power Generating Capacity (KWH/T−NaCl)		
	3-Effect	4-Effect	5-Effect	3-Effect	4-Effect	5-Effect
100	311	241	201	616	457	365
125	247	192	160	490	364	290
150	205	159	133	406	302	241
175	175	136	113	346	257	205
200	152	118	98	301	224	179
225	134	104	87	267	198	158
250	120	93	78	239	177	141
275	109	84	70	216	160	128
300	99	77	64	197	146	116
317 (saturated)	93	73	60	185	137	110

Evaporating crystallizer : Triple-effect. Electricity for pump etc. 120KWH/T·NaCl
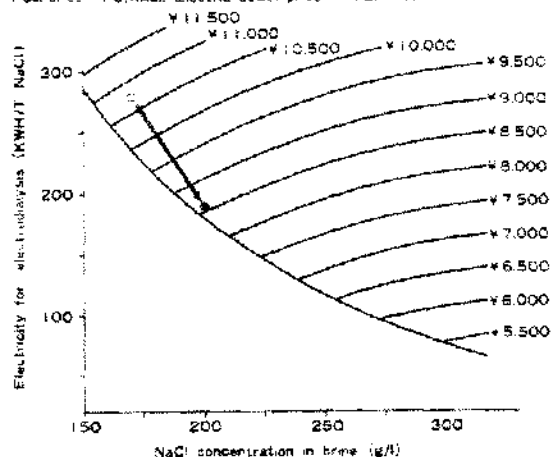Fuel price ¥6/Mcal. Electric power price ¥18/KWH

Figure 6. Energy cost of salt manufacturing.

Evaporating crystallizer · Triple-effect. Electricity for pump etc. 120KWH/T·NaCl
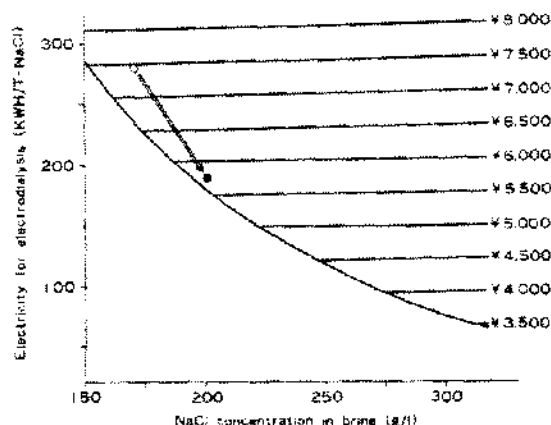Fuel price · ¥4/Mcal. Electric power price · ¥18/KWH

Figure 8. Energy cost of salt manufacturing.

Evaporating crystallizer Quintuple-effect. Electricity for pump etc. 130KWH/T·NaCl
Fuel price · ¥6/Mcal. Electric power price · ¥18/KWH

Figure 7. Energy cost of salt manufacturing.

Evaporating crystallizer · Quintuple-effect. Electricity for pump etc. 130KWH/T·NaCl
Fuel price : ¥4/Mcal. Electric power price ¥18/KWH
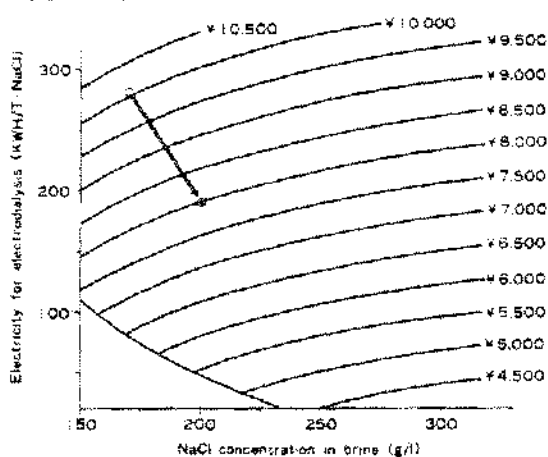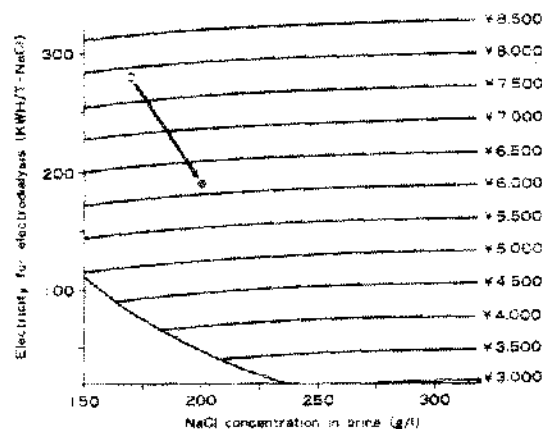
Figure 9. Energy cost of salt manufacturing.

comparison with the fuel price, then emphasis should be placed on improvements that reduce the electric power consumption. Conversely, where electric power is relatively cheap in comparison with the fuel price, the main development goal becomes the achievement of higher NaCl concentrations in the electrodialytic process.

Operation in Conjunction with Large Power Plants

Large-scale steam turbine power plants are commonly used throughout the world and can readily provide a low-cost supply of both the electricity and the low-pressure steam required for NaCl plants employing the ion-exchange membrane process. The combination of these two plants allows efficient utilization of waste steam and residual seawater from the power plant, off-peak or low-load generating capacities.

Utilization of Residual Steam. In the usual power plant, the steam discharge from the turbine is condensed by seawater or by utilization as low-pressure steam in chemical or other plants. Installation in these steam condensors of heaters for the evaporating crystallizer of the NaCl plant will result in more efficient utilization of fuel. This principle has been applied for a NaCl plant recently constructed by Asahi Chemical in the Republic of Korea, which is connected to a power plant. Although both the electric power and the steam from this power plant are utilized by a petrochemical complex, few of the plants in the complex could utilize its low-pressure steam. This tended to keep the generating costs high and prevented operation at full generating capacity. These problems have been eliminated by the NaCl plant, which now utilizes large amounts of the residual steam and contributes to efficient power generation.
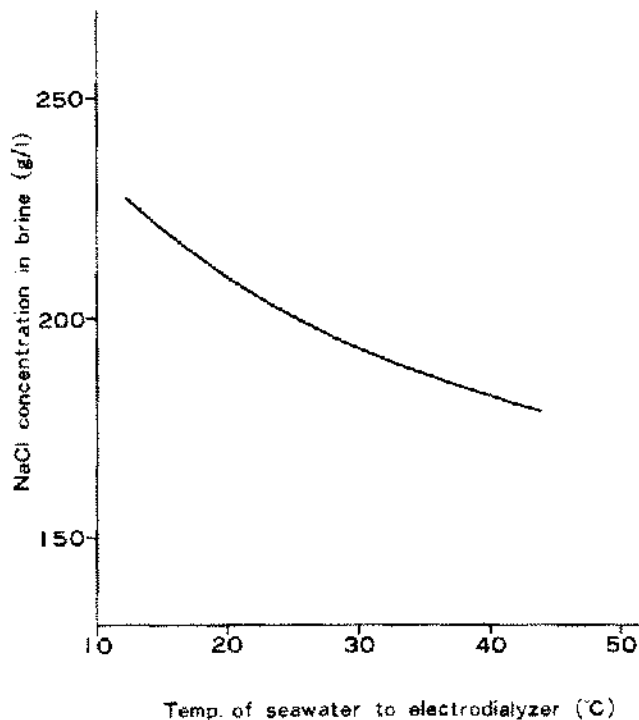
Figure 10. Relation of NaCl concentration in brine and temperature.

Figure 11. Relation of electric energy and temperature.

In order to allow the use of low-pressure steam by other new plants in this complex by reducing the NaCl plant steam consumption, planning is underway for replacement of the present triple-effect evaporating crystallizer of the NaCl plant with a quadruple-effect one.

Utilization of Residual Seawater. The seawater effluent from large power plants is commonly used in cooling processes and is thus elevated in temperature. The use of this heated seawater in electrodialysis can result in significant reductions in the energy cost.

The relation between the seawater temperature, brine concentration and power consumption is illustrated in Figures 10 and 11.

Although electrodialysis of seawater at 30°C, instead of usual 20°C, results in a lowering of the product brine concentration from 210 g/l to 190 g/l, this is more than offset by the reduction in unit power consumption, from 210 kWh/T—NaCl to 170 kWH/T—NaCl (Figures 6, 7, 8 and 9).

Utilization of Electric Power at Low-Load Hours. Unlike the conventional salt field processes, the basic nature of the ion-exchange membrane process makes night operation completely practical and thus allows more efficient utilization of power generating capacity through operation in off-peak or low-load periods.

Future Goals

Given the present levels of brine concentration obtained with the permselective ion-exchange membranes, the con-
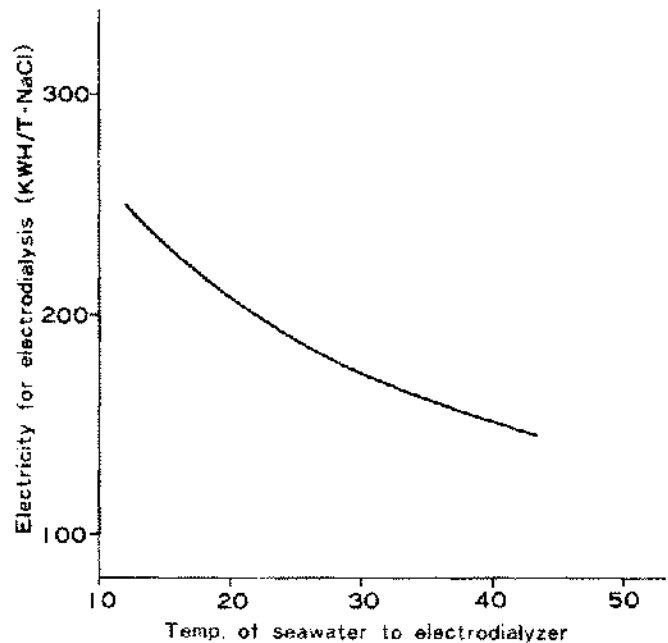
trolling factor in electric power consumption will remain the membrane and electrodialyzer efficiency. An important goal of research and development will therefore continue to be the further improvement of membranes and electrodialyzers, to achieve more efficient electrodialysis.

On the other hand, more complete integration of the salt plant with large power plants will be pursued, with development of equipment and process designs more closely tailored to take full advantage of the low-pressure steam and warm seawater available at very low cost from such power plants.

This may be followed ultimately by development of salt plants in which a far greater proportion of the overall energy requirement is met by the low-pressure steam from the large power plants, and a corresponding decrease in the level of electric power consumption for electrodialysis. This would mean the satisfaction of almost all of the energy requirements by an energy source that is available at virtually no cost.

In such plants, the brine would be concentrated almost entirely in evaporating crystallizers, with the concentration of the brine from the electrodialyzers being little different from that of seawater. However, it would be essential for these membranes to be highly permselective against the Ca, Mg, SO$_4$, CO$_3$ and other ions present in seawater which would otherwise cause severe scaling in the evaporating crystallizers. Although the present ion-exchange membranes efficiently prevent passage of these components where the electrodialysis results in relatively high NaCl concentrations, new membranes must be developed for economical permselective performance while obtaining low NaCl concentrations.

Thus, the primary requirement in such operations is for a membrane that provides a NaCl brine of high purity and achieves this permselectivity at a very low rate of electric power consumption, rather than one which provides a high level of brine concentration.

APPENDIX

*List of Commercial Applications
of Ion Exchange Membrane Technology
by Asahi Chemical Industry Co., Ltd.*

1. Salt manufacturing plants

1956   Start of the commercial operation of salt manufacturing plant from seawater by multi-effect vapor-compression method.

1973   Total capacity of salt factories in Japan using ACI's technology

Shin-Nihon Chemical Industry Co., Ltd.	186,000 MT/Y
Akoh Seawater Chemical Industry Co., Ltd.	175,000
Naruto Salt Manufacturing Co., Ltd.	184,300
Total	545,300 MT/Y

1975   Start of commercial operation of TESF (a corporation owned by Ministry of Economy) plant in Taiwan, Republic of China

(Table Salt: 110,000 MT/Y)

1979   Start of the commercial operation of HANJU (a corporation owned by Ministry of Commerce and Industry) Plant in the Republic of Korea

(Table Salt: 150,000 MT/Y)

2. Brackish water and seawater desalination

1961   Start of the commercial operation of brackish water desalination plant of the U.S. department of the Interior, in Webster, South Dakota, U.S.A.

(Tap water: 950 M^3/D)

1970   Start of the commercial operation of Shikine-jima brackish water desalination plant in Japan

(Tap water: 200 M^3/D)

1972   Start of the commercial operation of 1st Oshima brackish water desalination plant in Japan

(Tap water: 1000 M^3/D)

Start of operation of brackish water desalination plant at Brindisi in Italy

(Tap water: 1200 M^3/D)

1974   Start of the commercial operation of 2nd Oshima brackish water desalination plant in Japan

(Tap water: 1000 M^3/D)

Start of the commercial operation of Noshima seawater desalination plant in Japan

(Tap water: 120 M^3/D)

3. Whey desalination

1975   Start of the commercial operation of Morinaga Milk Industry Plant in Japan

(8 M^3—Whey Solution/hr)

1976   Start of the commercial operation of Milei Plant in W. Germany

(13.7 M^3—Whey Solution/hr)

4. Adiponitrile production

1971   Start of the commercial operation of Asahi Chemical Industry Plant in Japan

(25,000 MT/Y)

1984   Start of the commercial operation of Rhodia Nordeste S.A. Plant in Brazil

(30,000 MT/Y)

5. Uranium reduction

1961   Start of operation of Japan Atomic Fuel Corp. Plant in Japan

(4.2 kg/hr)

1972   Start of operation of pilot plant at Ningyo-toge in Japan

(100 MT—UF_6/Y)

1981   Start of the commercial operation at Ningyo-toge in Japan

(2 MT—U/D)

6. Caustic soda production

1975   Start of the commercial operation of 1st Asahi Chemical Industry Plant in Japan

(80,000 MT/Y)

1976   Start of the commercial operation of Denki Kagaku Plant in Japan

(60,000 MT/Y)

1978   Start of the commercial operation of Prince Albert Plant in Canada

(30,000 MT/Y)

1979   Start of the commercial operation of St. Anne Plant in Canada

(10,000 MT/Y)

1981   Start of the commercial operation of N.Z. Forest Products Plant in New Zealand

(10,000 MT/Y)

1982   Start of the commercial operation of 2nd Asahi Chemical Industry Plant in Japan

(40,000 MT/Y)

1983   Start of the commercial operation of Akzo Zout Chemie Plant in Netherlands

(280,000 MT/Y)

Start of the commercial operation of Tasman Pulp & Paper Plant in New Zealand

(10,000 MT/Y)

7. Other applications

Asahi Chemical Industry has supplied to various companies ion exchange membrane technology and equipment for the fields of chemicals and food products.

1979 Start of the commercial operation of re-use plants of color developer in Japan

($0.2 \, m^3/hr$ and $1 \, m^3/hr$)

Start of the commercial operation of desalination of wine in Japan

($1.5 \, m^3/hr$)

1981 Start of the commercial operation of desalination of cane sugar syrup in Japan

($80 \, m^3/D$)