

Concentration of Sea Water by Electrodialysis with Ion-Exchange Membranes

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ABSTRACT

This paper outlines the present technique of concentration of sea water by electrodialysis with data obtained at several test plants and reports following points of those results obtained at Odawara Salt Experiment Station of the Japan Monopoly Corporation:

newly developed gaskets which are capable of using the effective area of membranes.

the structure of a spacer which unifies the concentration of sea water in the diluting compartment, by avoiding scale deposit, the greatest obstacle in operation.

data showing the effects of temperature and concentration of magnesium contained in brine on the deposit of calcium carbonate.

data showing the effects of current density, temperature and concentration of sea water upon concentration and composition of brine, and power consumption.

In addition, this paper will explain future problems as to how to decrease the cost of salt production, for example, an increase in the operating current density, an improvement of membrane selectivity to univalent ions, the utilization of by-products, and a combination of a dual purpose (power generation and desalination) and salt production with ion-exchange membranes.

INTRODUCTION

Because Japan has a high annual rainfall and no material other than seawater, salt has been produced either by obtaining brine from a type of

salt-field peculiar to Japan and then passing it through evaporators or by passing seawater itself through a series of evaporators. The evaporators used in either method, which require the removal of 40 tons of water to obtain one ton of salt, are of the multiple-effect vacuum or thermo-compression systems or a combination of both. Recently, we have succeeded in developing a technique of concentrating seawater by electrodialysis with ion-exchange membranes. This requires less energy consumption and results in brine of higher concentration irregardless of weather conditions.

Some salt plants have been producing brine by means of electrodialysis apparatus as well as salt-fields. The total quantity of salt in brine obtained by the electrodialysis process at six test plants has risen to approximately 120,000 tons a year, or 13% of the total quantity of salt produced in Japan.

The salt industry is governed by the Monopoly Law from production to sales, and salt research has been carried out by the Japan Monopoly Corporation. This paper deals with the present situation regarding the new concentrating technique, the experimental results obtained at our station, and the future problem of decreasing salt production cost.

PRINCIPLE AND FLOWSHEET

The principle of concentration of seawater by electrodialysis is shown in Figure 1. The apparatus consists of a series of alternate concentrating and diluting compartments formed by alternate cation- and anion-exchange membranes. Seawater is introduced to the diluting compartments and an electric potential is applied between the electrodes. Move-

ment of the cations and anions, accompanied by hydration water, takes place toward the cathode and anode. Brine can be obtained in alternate concentrating compartments through permselectivity of the membranes.

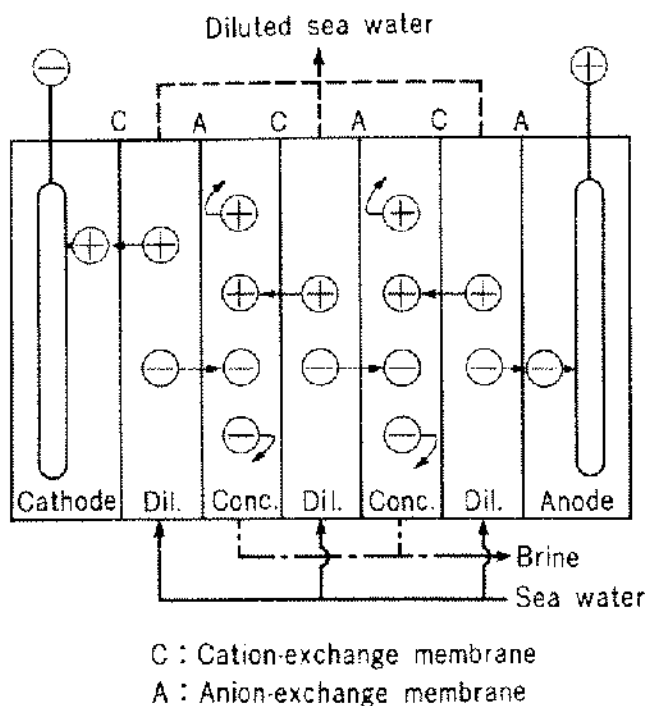


Figure 1. Principle of concentration by electrodialysis.

An example of an electrodialysis process flowsheet is shown in Figure 2. Seawater is sent to the sand filter, either directly or after preheating at the barometric condenser connected with the last vac-

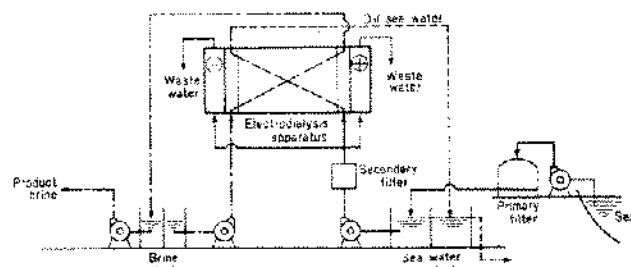


Figure 2. Flowsheet of electrodialysis process.

uum evaporator. Then, if necessary, the water is sent to the secondary filter so that any suspended matter may be removed. It is then passed to diluting compartments where it is desalted while flowing upward with a velocity of 4-6 cm/sec. After being recycled in the system, it is discharged with a concentration 65-80% that of the seawater supplied. Seawater also is introduced to the electrode rinse compartments, and acid may be added to the cathode rinse in order to prevent magnesium hydroxide precipitation or remove precipitates in the compartment. If necessary, brine obtained may be recycled, before it is supplied to the evaporators, as shown in the figure in order that scale inhibitor may be added.

ION-EXCHANGE MEMBRANE

The characteristics of conventional Japanese ion-exchange membranes for concentration of seawater are shown in Table 1. Membrane permselectivity in regard to certain ions among those of the same charge is extremely important as it has a di-

Table 1. Characteristics of Ion-exchange Membranes.

Maker and name of membrane	Type	Backing	Thickness (mm)	Specific resistance (Ω cm)	Transport number	Remarks
Ac	styrene-butadiene copolymer					
CSV	strongly acidic	yes	0.22~0.25	120~180	0.93	for unit cell type
AST	strongly basic	yes	0.20~0.23	290~350	0.95	
T	styrene-divinylbenzene copolymer					
CLS-2.5T	strongly acidic	yes	0.15~0.17	160~210	0.98	do.
AVS-4T	strongly basic	yes	0.15~0.17	220~310	0.98	
Ac	styrene-divinylbenzene copolymer					
CK-2	strongly acidic	no	0.23	143	0.91	for filter press type
CA-3	strongly basic	no	0.21	111	0.98	

rect bearing on the formation of scales on membrane surfaces. In particular, the only way to prevent calcium sulphate scale is by reducing membrane permselectivity in regard to either or both calcium and sulphate ions. This results in causing less ionic product of calcium and sulphate than the solubility product on the surface of the membrane in the concentrating compartment. Research, therefore, has been concentrated on development of membranes of low permselectivity to bivalent ions, i.e., high permselectivity to univalent ions. Several firms have succeeded in developing such membranes, and these have resulted in prevention of scale formation, an increase in current efficiency where sodium chloride is concerned, and rapid progress in concentration of seawater. However, all require periodic retreatment after being placed in use.

ELECTRODIALYSIS APPARATUS

There are two types of electrodialysis apparatus in practical operation; the unit cell type and the filter press type. In the *unit cell type*, a cation membrane and an anion membrane are patched together along their margins to form a bag, as shown in Figure 3, called the unit cell. The seawater flows upward between the cells and the brine permeating into them is drawn out through the hoses connected with the brine inside the cells. A membrane stack consists of tens of alternate cells, intermembrane spacers and frames. Tens of stacks are placed on shelves in the electrodialysis box made of hard PVC. The characteristics of this type of apparatus are as follows; it is simple in construction and membrane spacing is relatively wide, about 1 mm, and therefore placing of the stacks in, or removing them from, the box is a simple matter. Further, the apparatus can operate for a long period without being affected by matter suspended in the supplied seawater. Air jets introduced through nozzles in the bottom of the box agitate the seawater and help to dislodge suspended matter from the membranes.

In the *filter press type*, alternate cation and anion membranes are inserted between gaskets made of non-conducting material such as rubber or PVC, as shown in Figure 4 (Sugi, 1968, p. 10). Hundreds of membranes, intermembrane spacers and gaskets, pressed between fastening frames, form a membrane stack. Several stacks are assembled like a filter press. Seawater is supplied to and discharged from the diluting compartments through conduits formed by a series of holes in

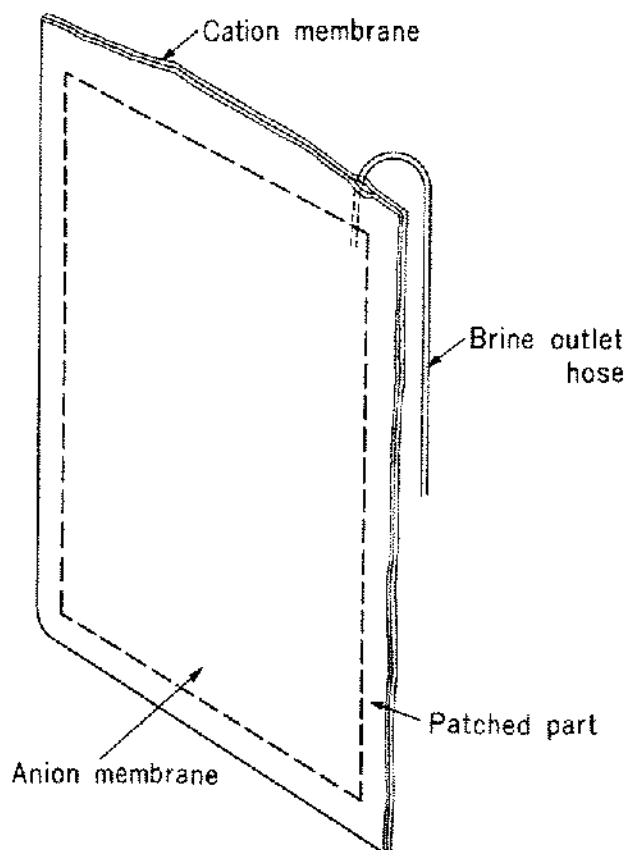


Figure 3. View of unit cell.

gaskets and membranes. As the apparatus in Figure 4 is for experimental use, it is possible for the brine in each concentrating compartment to be separately withdrawn and not recycled.

In apparatus for commercial use, however, the brine from the separate concentrating compartments flows out together and can be recycled like seawater in diluting compartments through conduits as shown in the lower part of Figure 5. The characteristics of the filter press type electrodialysis apparatus are contrary to those of the unit cell type; membrane spacing is narrow, about 0.75 mm, and electric resistance between electrodes is low but apt to be affected by suspended matter in the seawater.

In the conventional type of gaskets, the external dimensions are about the same as those of a membrane and conduits are formed by the holes in them. If the former is made larger than the latter, and either or both the holes which form conduits for seawater or brine are contained in the gaskets alone, a greater membrane surface area becomes

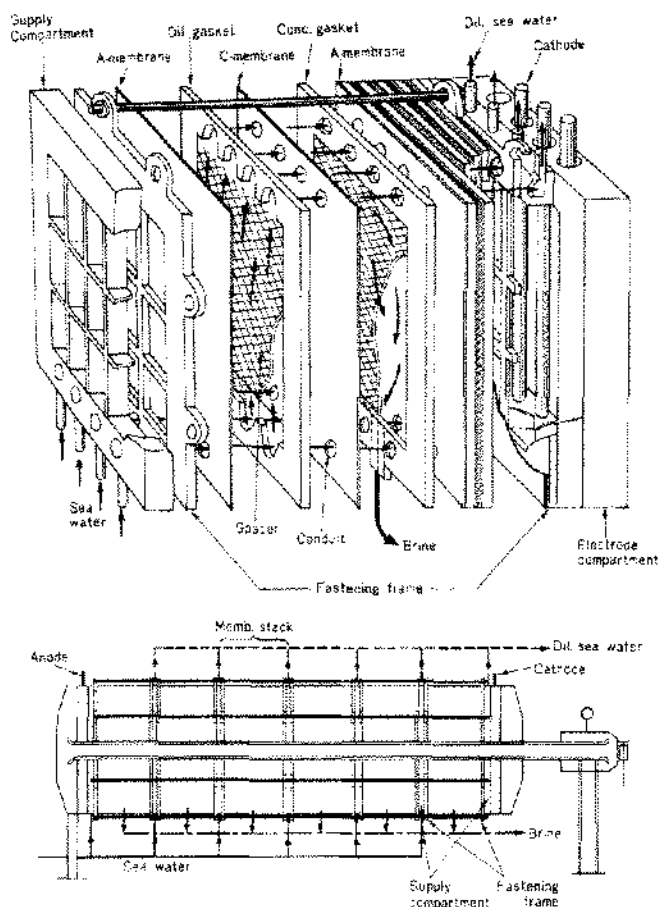


Figure 4. Structure of filter press type apparatus.

available. An example of such gaskets recently developed is shown in the upper part of Figure 5 (Kaho et al., 1969) where membranes have holes for brine conduits alone. This improvement in the structure of gaskets resulted in an increase of about

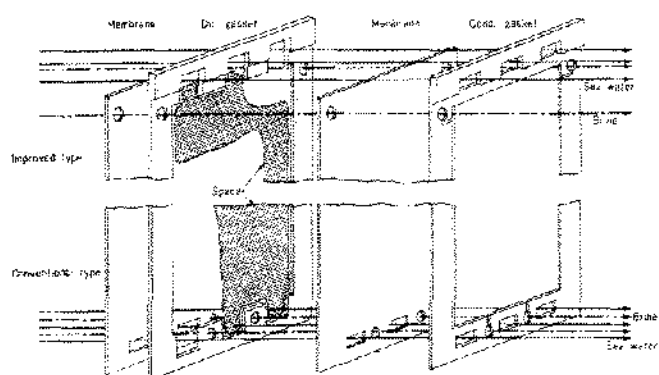


Figure 5. Structure of gaskets.

10% in the effective membrane area and a decrease of membrane and capital costs in brine production.

In commercial apparatus, the membrane area is 1-1.3m², and usually a filter press type apparatus has 1,500 pairs of membranes (6 membrane stacks, 250 pairs per stack) while the unit cell type has 600 pairs (30 stacks, 20 pairs per stack).

TROUBLES ENCOUNTERED AND OPERATIONAL DATA

Scale formation. The most important problem that has to be overcome in operation is scale formation on membranes. Such scale causes not only an increase in the electric resistance but also obstructs the liquid flow, leading to scale formation in adjoining compartments one after another and finally blocking operation of apparatus.

Scale can be classified into two groups by causes: one appears as calcium sulphate or calcium carbonate in the concentrating compartments when the ionic product in brine exceeds the solubility product, and the other appears as magnesium hydroxide or calcium carbonate in both the concentrating and diluting compartments when smooth liquid flow is prevented or local overcurrent caused, leading to pH change in the diluting compartments (Hanzawa et al., 1965, p. 47-52).

Calcium sulphate scale, however, gives little trouble at present because of the improvement in membrane permselectivity. Calcium carbonate deposited due to the first cause was found closely related to the concentration of magnesium in and temperature of brine as shown in Figure 6 (Yamamoto and Yugi, 1969). However, it can be satisfactorily prevented by adding 10-20 ppm of

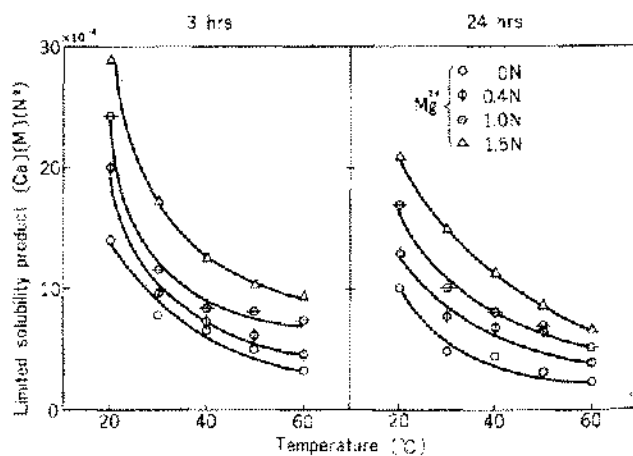


Figure 6. Effects of concentration of magnesium in and temperature of brine on deposit of calcium carbonate.

lyphosphate to the brine recycled in the filter press type apparatus, or by acidifying the supplied seawater in the unit cell type.

The best way to prevent scale formed by the second cause, i.e., pH change is to have uniform fluid flow in the diluting compartments. Inter-membrane spacer material research was carried out with successful results. The stream lines resulting from either the recently developed diagonal net spacer or the conventional honeycomb net spacer used are shown in Figure 7 (Hanzawa et al., 1965, p. 16-25).

The diagonal net spacer, molded from polyethylene, has one group of parallel strands arranged

on another similar group at a definite angle. Compared with the conventional spacer, the diagonal net spacer completely mixes the stream lines with small frictional pressure loss. This spacer is applicable to both types of apparatus, and especially for the filter press type with narrow membrane spacing.

Deposited matter. Even if sufficient filtration of seawater and prevention of scale formation are carried out, the apparatus should be stopped for inspection after a fairly long period of operation. In the filter press type, 0.1-0.2 ppm of suspended matter in the filtrated seawater gradually increases the frictional pressure loss in diluting compartments. Membrane stacks are disassembled so that matter deposited on membranes and spacers may be washed off every 2-4 months, split membranes repaired or replaced with others, and the little quantity of magnesium hydroxide and calcium carbonate sometimes deposited on membranes dissolved with acid. In the unit cell type, membrane stacks are not disassembled as often as in the filter press type. An example of quantity and composition of deposited matter in the diluting compartments of the filter press type is shown in Table 2 (Watanabe et al., 1969).

Since the high permselectivity to univalent ions of cation membranes, used in both types of apparatus, decreases with time, the membranes are retreated when the stacks are disassembled.

Operational data. The first year's operational data for two representative test plants are shown in

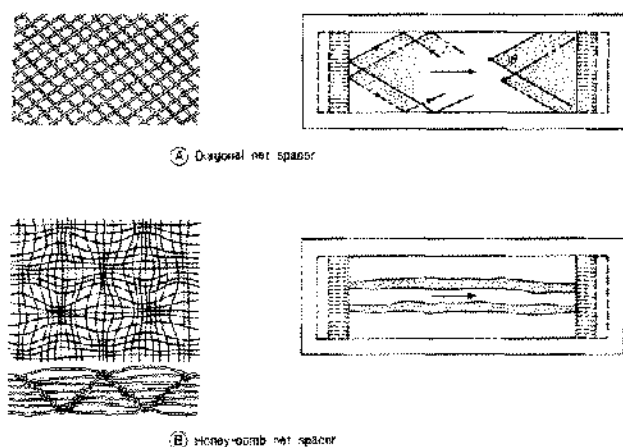


Figure 7. Structure of spacers and stream lines through them.

Table 2. Quantity and Composition of Deposited Matter in Diluting Compartment.

Sampling part		Quantity of deposited matter (g/m ²)	Rate of deposition (mg/m ² h)	Soluble matter for acid (%)		Remarks
				Fe(OH) ₃	8.0~10.1	supplied sea water suspended matter: 0.1ppm flowrate: 120l/h (4cm/s) operating time: 1,392hrs
Cation membrane		2.10/6.27	0.24	ignition loss	18.2~24.7	
Anion membrane		3.34/6.27	0.38	the others	9.1~13.0	
Spacer		14.11/6.60	1.54	subtotal	37.1~45.7	
Total		————	2.16	Insoluble matter for acid (%)		
Cation membrane	(1)	0.28/0.10	2.00	moisture	1.3~ 2.7	(1) liquid distribution slots (2) lower part (3) upper part
	(2)	0.54/0.62	0.63	ignition loss	15.4~16.7	
	(3)	1.44/5.63	0.18	SiO ₂	24.3~27.8	
Anion membrane	(1)	0.25/0.10	1.79	Fe ₂ O ₃	1.7~ 2.1	
	(2)	0.78/0.62	0.91	Al ₂ O ₃	6.5~12.3	
	(3)	3.26/5.63	0.42	the others	0.9~ 4.0	
Spacer	(1)	1.11/0.11	7.48	subtotal	54.3~62.9	
	(2)	4.59/0.65	5.09			
	(3)	10.00/5.93	1.21			

Table 3. Operational Data at Test Plants.

Test plant	Current density	Supplied sea water		Product brine					Electric power consumption
		temperature	concentration	pH	concentration		quantity		
	A/dm ²	°C	N/Cl		N/Cl	N/NaCl	10 ³ kl	10 ³ l/NaCl	
A	3.61	22.3	0.496	7.2	3.21	2.85	198.1	32.99	295
K	1.69	23.2	0.500	5.5~6.7	3.34	2.85	139.6	23.28	293

Table 3. Plant A has 5 units of filter press type apparatus, and one unit, about 1,500 pairs of membranes without backing, has been operated at a current of about 360A and a potential of about 650V. Plant K has 16 units of unit cell type apparatus, and one unit, about 600 pairs of membranes with backing, has been operated at about 200A and 250V. The operation in these plants has been performed with safety and stability.

FUTURE PROBLEMS

Current density. Before discussion of future problems, the relation between current density and the cost of salt production will first be considered. The cost of salt production consists of concentration cost and crystallization cost. And the concentration cost reaches a minimum at a certain value of current density, i_B (Wilson, 1960, p. 234-243). On the other hand, the concentration of brine obtained increases with current density, and both the degree of evaporation required for crystallization of brine and the crystallization cost gradually decrease. Therefore, the cost of salt production also reaches a minimum at a certain current density, i_S , as shown in Figure 8. In the figure, i_S is larger than i_B . Please note that as a precautionary move, the operating current density is being kept at less than i_B , while it is considered that one of the best ways to decrease the cost of salt production is to increase the operating current density, although it may be necessary when doing this to carry out further action to prevent increased scaling caused by pH change.

Permselectivity of membranes. Among improvements made in membrane characteristics, permselectivity to univalent ions is the most important. Some membranes of late have resulted in brine in which sodium chloride accounted for 90% of all salts contained therein on a weight basis. This resulted in increases in effective current and brine output, and in reducing scale prevention in the crystallization process because of less scale composition in brine. However, one problem is that the

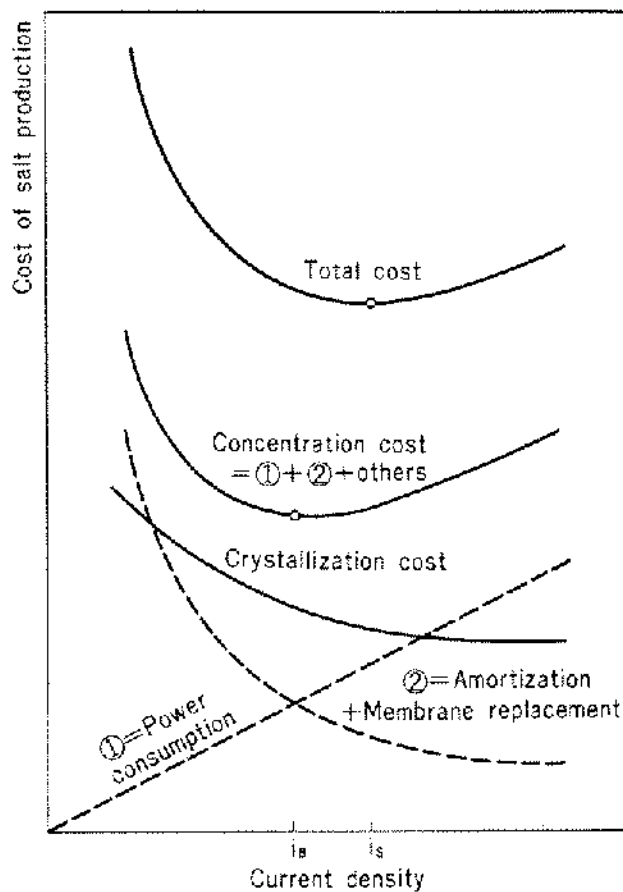


Figure 8. Relation between cost of salt production and current density.

permselectivity imparted to membranes through re-treatment becomes ineffective in several months after each treatment. Also, special care must be taken during the evaporation process to avoid deposits of potassium chloride. (Matsuo and Tenjin, 1967, p. 90-98).

Unit prices of energies. The concentration process requires D.C. power for electrodialysis and a little A.C. power for motors. The crystallization process requires steam for evaporation and a little

power for motors. Therefore, it is planned to decrease unit prices of required energies by generating electric power as well as steam with an extractor or a back pressure turbine in the salt plant.

Temperature and concentration of supplied seawater. Effects of temperature and concentration of supplied seawater on concentration characteristics are shown in Figure 9 (Kaho et al., 1969). The effects of temperature and concentration of seawater

when desalination of seawater by the flash evaporation process is realized. This suggests the necessity for combination of a dual purpose plant, for power generation and desalination, and a salt plant with ion-exchange membranes.

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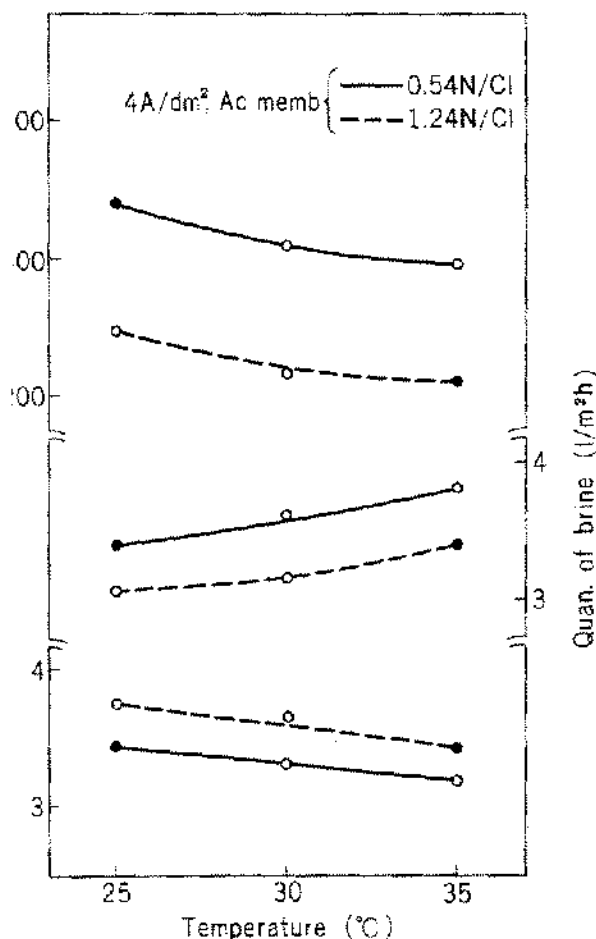


Figure 9. Effects of temperature and concentration of supplied seawater on concentration characteristics.

displaced each other out and the concentration and quantity of brine was not changed, but electric power consumption sharply decreased. It is believed that higher temperature and concentration would make operation at higher current density possible and considerably decrease the cost of salt production, with little effect on the life of membranes at temperatures of up to 40°C. Although it is now impossible to obtain such concentrated seawater commercially, it will be easy in the future