

Modernization of Salt-Manufacturing Process by Electrodialysis Using Ion-Exchange Membrane Technology

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ABSTRACT

Asahi Chemical Industry has carried out research and development on ion-exchange membrane technology as well as on the applied process since 1950. As a result of these efforts, Asahi Chemical Industry established the process of manufacturing salt from seawater by electrodialysis using the ion-exchange membrane. The company has the world's largest production capacity by this method and produced 685,000 metric tons a year in 1977.

The paper presents a summary of the general method of electrodialysis and a detailed explanation of the performance of plants which are in operation. In addition, data on the economics and conditions for application of the process are described in detail. The process is applied to both the desalination of seawater and the demineralization of brackish water.

MODERNIZATION OF SALT MANUFACTURING PROCESS IN JAPAN HISTORY

In the past, salt for food use in Japan was mainly produced by solar processes at a salt field. All the salt manufacturing using salt fields were converted to the ion-exchange membrane process and there are no more salt fields in Japan. By the adoption of this process, the Japanese salt industry emerged from a traditional salt producing methodology similar to agriculture into a modern chemical industry. The current salt consumption in Japan is tabulated in Table 1 which shows individual consumption by usage.

In 1960 all the salt produced in Japan was produced by the salt field method. About 6,000 workers were working in salt fields, totalling about 3,000 hectares, to produce about 800,000 metric tons of salt per annum. The Japanese Government and the Japan Tobacco and Salt Public Corporation since 1961 have been studying salt manufacturing policy in Japan. With our establishment of the ion-exchange mem-

brane process, the government in 1971 enacted a law under which salt fields were to be totally abolished. The salt manufacturing process using ion-exchange membranes was declared as the only process for the salt manufacture. As a result, in 1972, the salt manufacturing business in Japan was unified into seven producers and there was a total switchover to the ion exchange membrane process. Because the area of a modern plant is only 1/100–1/600 of that of solar process plant, the vast lands which formerly were salt fields are being converted into industrial sites, fish nurseries, agricultural lands and other social purposes. Furthermore, the number of workers has been reduced to 5–10% of that required for the solar processing plants. Table 2 shows the present salt manufacturing plants using electrodialysis in Japan.

Asahi Chemical's role in the salt modernization. Asahi Chemical has worked assiduously since around 1950 on the development of ion-exchange membranes. These are mainly for seawater concentration as well as for the elec-

TABLE 1
Annual Salt Consumption in Japan (as of 1976)

	Pure Refined Salt MT	Common Grade Salt (Refined) MT	Crash or Raw Salt From Abroad MT	Total MT
For homes	34,572	435,976	11,402	481,950
For food industries	20,205	596,060	511,275	1,127,540
For industries besides food industries	1,176	150,382	158,334	309,892
For others	520	137,720	7,628	145,868
Total	56,473	1,320,138	688,639	2,065,250

TABLE 2
Salt Manufacturing Plants Using Electrodialysis in Japan

Name of the Company	Production Capacity (Metric Ton-Salt/Y)	Technology
Shin Nihon Chemical Ind. Co.	186,000	Asahi Chemical
Ako Sea Water Chemical Ind. Co.	175,000	Asahi Chemical
Naruto Salt Mfg. Co.	184,300	Asahi Chemical
Naikai Salt Works	192,000	Asahi Chemical Asahi Glass
Sakito Salt Works	179,000	Asahi Glass
Kinkai Salt Mfg. Co.	173,000	Tokuyama Soda
Sanuki Salt Mfg. Co.	172,700	Tokuyama Soda
Total	1,262,000	—

trodiolizers in which the membranes are used. Asahi Chemical also has carried on developmental work on the evaporating crystallization of concentrated brine. In 1958, Asahi Chemical installed a pilot plant for the manufacture of salt by the ion-exchange membrane process in Nobeoka, Kyushu. Here tests and experiments were conducted prior to the commercialization of the technology. With approval of the Japan Tobacco and Salt Public Corporation, Asahi Chemical in 1961 built a commercial salt plant by the ion-exchange membrane process at Onahama, Fukushima Prefecture. It has a capacity of 50,000 metric tons per year. This pioneering Onahama plant is still in smooth operation as the oldest salt manufacturing plant by electrodialysis. The capacity of the electrodialyzers installed at that time has since increased by more than 20% by the improvement of technology.

A number of technical improvements were achieved at this plant with the result that Asahi Chemical's salt manufacturing process using ion-exchange membranes is now known as an industrially established technology. The history of the development of the ion-exchange membrane pro-

cess and its application by Asahi Chemical is chronologically tabulated in the Appendix at the end of this paper.

At present, the quantity of salt produced by the Asahi Chemical's salt manufacturing process accounts for nearly 50 percent of the total salt production of Japan. In addition to the plants abroad, including a plant under construction, Asahi has nearly 60 percent of the total salt product by use of ion-exchange membrane in the world. Asahi Chemical's technology, which has been accumulated over the years since 1950, covers the whole field of the salt manufacturing plant system, from intake of seawater as raw material to the packaging of finished product salt. In addition, the technology covers the utility facilities including supply of steam and power.

Principle of salt manufacturing process from seawater. In order to obtain salt from seawater, there are three possible processes. The salt field method (Case 1) produces salt from seawater only using solar energy. The modified salt field method (Case 2) concentrates seawater up to a certain level by solar energy and later crystallizes salt by evaporating the concentrated seawater using another

energy, such as steam. The ion exchange membrane process (Case 3) produces NaCl rich brine from seawater by means of electrodialysis using ion exchange membranes and crystallizes salt by evaporating the brine using steam.

Figure 1 illustrates the difference between these 3 cases. With Case 1, salt production costs will be low depending on

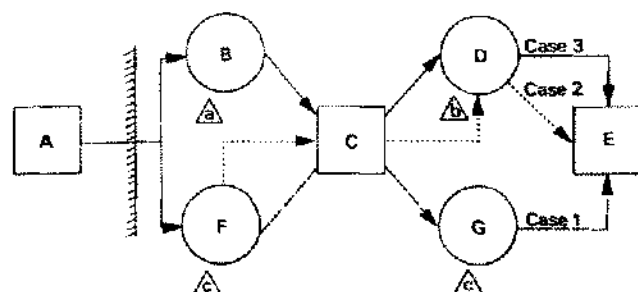


Figure 1. Salt manufacturing system from seawater. A, Seawater. B, Electrodialyzer. C, Brine. D, Evaporating crystallizer. E, Salt. F, Salt field. G, Salt field. Triangle a, Electrical energy. Triangle b, Thermal energy. Triangle c, Solar energy.

the site and weather conditions. However one cannot expect a high quality salt product and the production rate is subject to the weather conditions. With Case 2, the production rate is not constant because it depends on the weather, as with Case 1. A better quality will be expected than with the former case, but there will be difficulty in evaporating crystallization because scaling components in seawater are almost proportionally concentrated. The process in Case 3 is a unique technique developed by Asahi Chemical which enables one to industrially produce salt from seawater, regardless of the weather conditions.

Ion-exchange membrane process. The ion-exchange membrane process is also called the electrodialysis process when the process is used to concentrate or dilute salts in the solution. The principle of the process is as shown in Figure 2.

There are two kinds of ion exchange membranes, anion exchange and cation exchange membranes. In Figure 2, A and C stand for these membranes respectively. The anion exchange membrane permits the passage of only anions such as Cl^- . The cation exchange membrane permits the

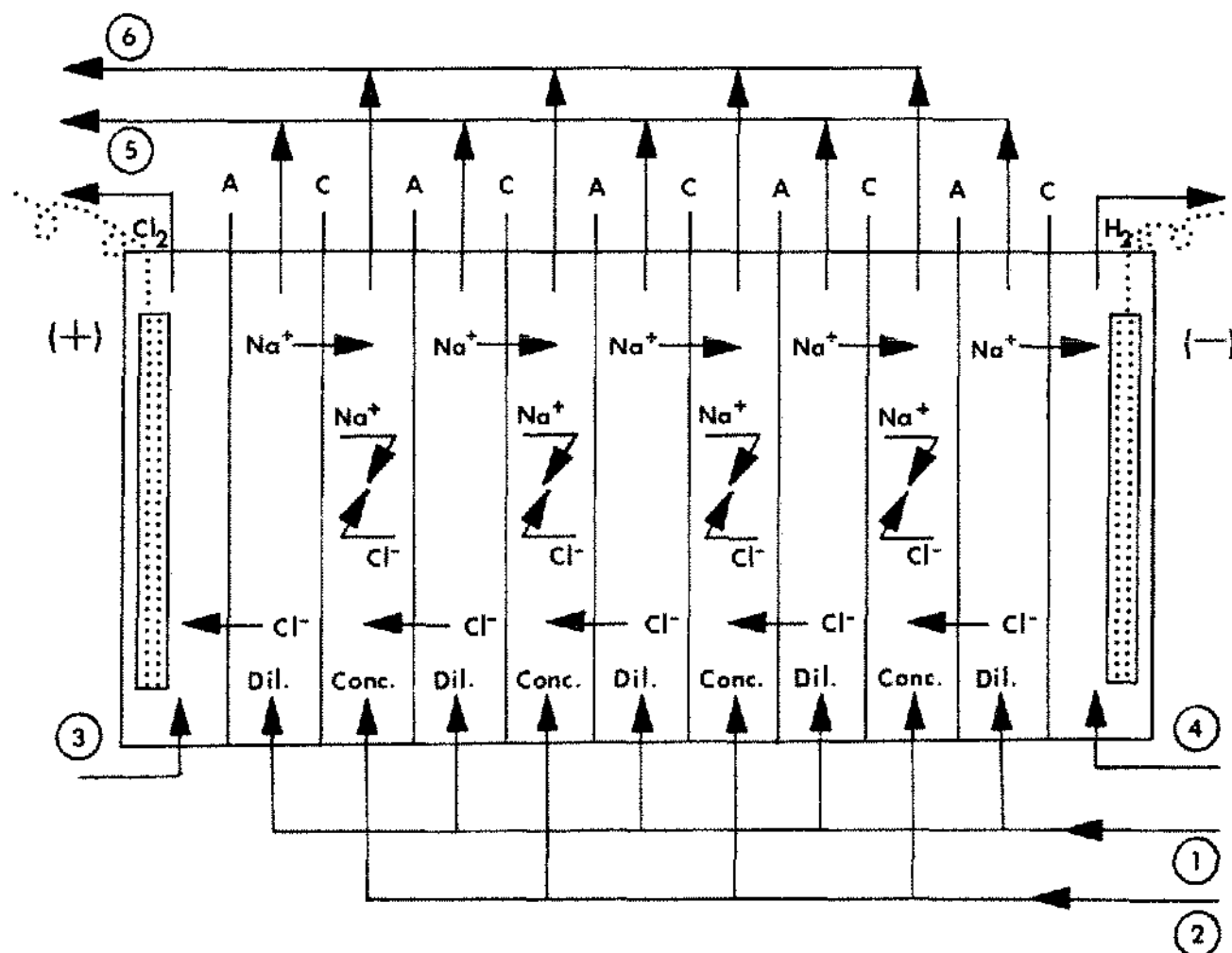


Figure 2. Principle of electrodialysis. 1, Inlet of dilution stream. 2, Inlet of concentration stream. 3, Anode compartment stream. 4, Cathode compartment stream. 5, Outlet of dilution stream. 6, Outlet of concentration stream.

passage of only cations such as Na^+ . The equipment consists of two kinds of membranes alternately arranged as shown in the figure with a set of electrodes at both ends.

When the compartments partitioned by the membranes are filled with seawater and a direct electric current is passed between the electrodes, anions (Cl^-) and cations (Na^+) move toward the anode and the cathode respectively. Due to the existence of ion exchange membranes, anion and cation are concentrated or diluted as shown in the figure. As a result the equipment can be used either as a concentrator or as a diluter. Asahi Chemical not only developed ion-exchange membranes but also the equipment, i.e. the electrodialyzer. Both are suitable to the seawater concentration system.

A unique feature of the system is the use of monovalent selective ion-exchange membranes which have better permselectivities for monovalent ions such as Na^+ and Cl^- than those of divalent ions such as Ca^{+2} , Mg^{+2} and SO_4^{-2} . By using these membranes, the efficiency of the electrodialyzer is increased and the scaling trouble is decreased in the process of evaporating crystallization. This is because the brine produced by electrodialysis contains less scaling components than that produced at a salt field.

Figure 3 shows a picture of electrodialyzers in a salt manufacturing plant. Each unit contains as many as 3,600 sheets of ion-exchange membranes between a set of electrodes and is capable of producing brine which is equivalent to 11,000 metric tons of salt per year.

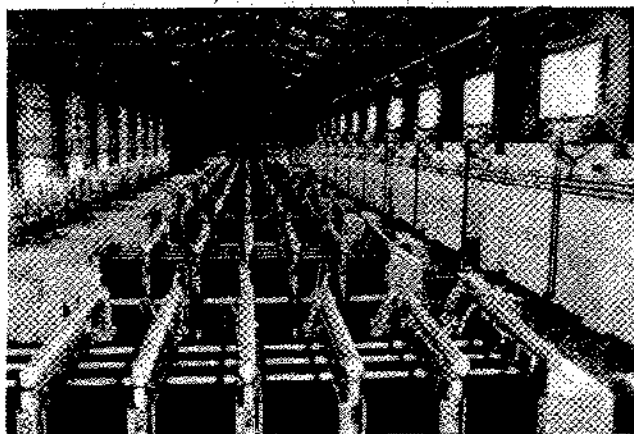


Figure 3. SS-O model electrodialyzers.

Description of Asahi Chemical's process. Salt manufacturing processes by electrodialysis are divided into four main parts: electrodialysis, evaporating crystallization, drying and packing and power and steam generation. The

electrodialysis section includes seawater intake and its pretreatment. A typical flowsheet of the process is shown in Figure 4 (except drying and packing).

Electrodialysis. Seawater taken in is partly used for the barometric condenser in evaporating crystallization and the rest is sent to pretreatment. As shown in the figure, after the barometric condenser, warmed seawater may be used to feed the electrodialysis. In actual operation, warmed seawater is utilized in winter to minimize the change of the seawater temperature all year round because the operating conditions of electrodialysis are affected by the change of seawater temperature.

Sand filtration is typical and sufficient as the pretreatment for electrodialysis. Sand filters of valveless type with automatic backwash are generally used and have been working satisfactorily for years. Filtered seawater is fed to the dilution pit and is fed to the electrodialyzer. The effluent from the electrodialyzer is partially desalted seawater and is discharged from the dilution pit while its portion is recycled.

Another stream to the electrodialyzer is the concentration stream where salt from seawater is collected during electrodialysis. As ions or salt permeates with a small amount of water, salt is collected in the form of brine in the stream and the brine is overflowed to the brine pit. The produced brine in the electrodialysis section is then fed to the evaporating crystallization section.

Evaporating crystallization. Salt in the brine from the electrodialysis section is crystallized by evaporating crystallizers. Triple effect evaporation is shown in the figure and the amount of the effect depends on the plant capacity. The evaporating crystallizer is of the external heating with reverse forced circulation type and special design is introduced to separate salt from impurities such as CaSO_4 . Bittern and impurities are continuously discharged out of the system.

Salt is drawn from the evaporating crystallizer as slurry and is separated by the centrifuge. Salt from the centrifuge ordinarily contains 1.5 to 2.5% of moisture and may be used as a product or may be sent to the drying section. Figure 5 is the triple effect evaporating crystallizer at a salt manufacturing plant.

Drying and packing. There are two types of drying methods: the fluidized bed and the pneumatic conveying types. The pneumatic conveying type developed by Asahi Chemical is cost and space saving and has been in smooth operation.

The authors omit an explanation of the packing system because it is well known and depends on the style of the product. Table 3 shows a typical analysis of product salt.

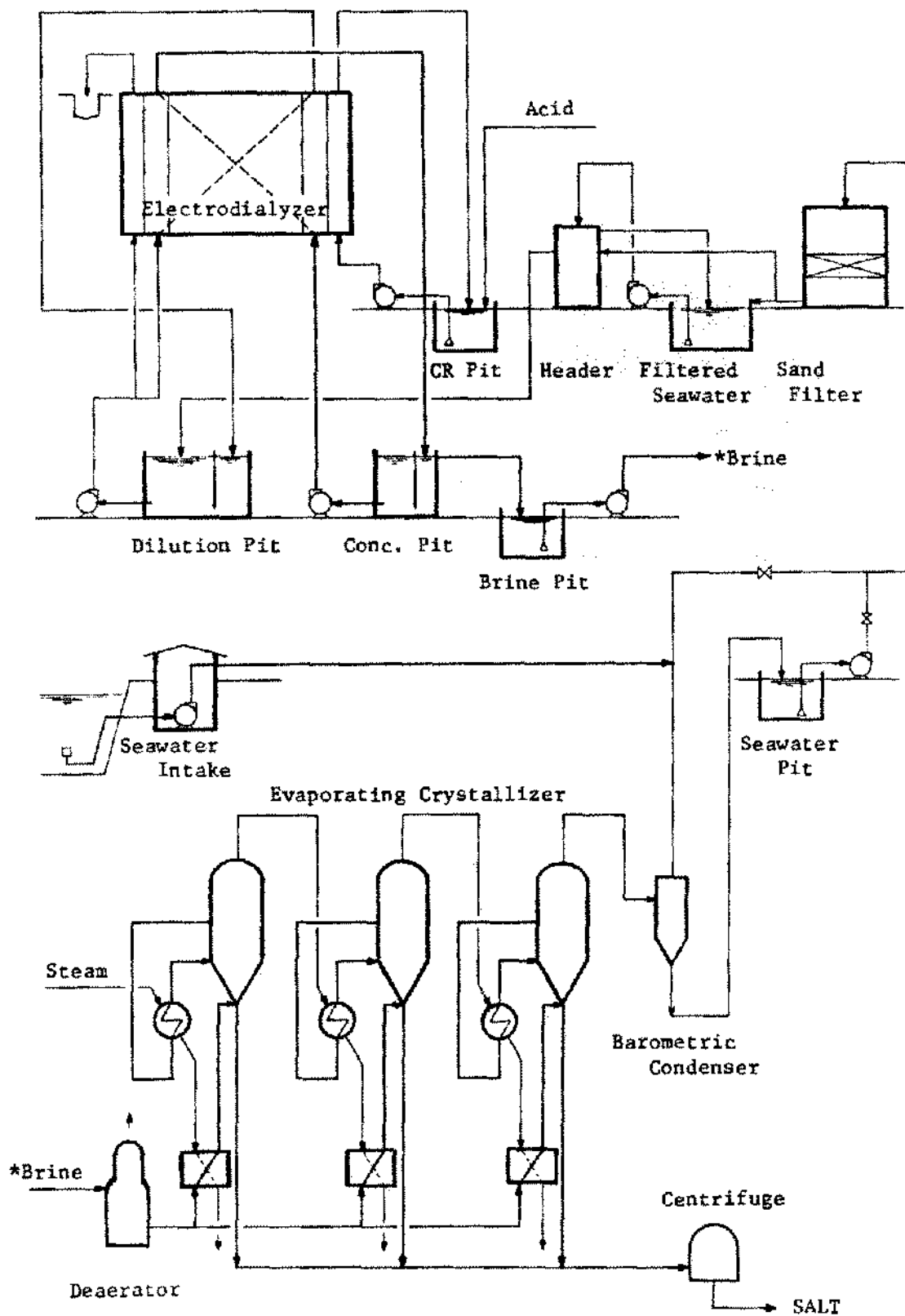


Figure 4. Salt manufacturing by electrodialysis.

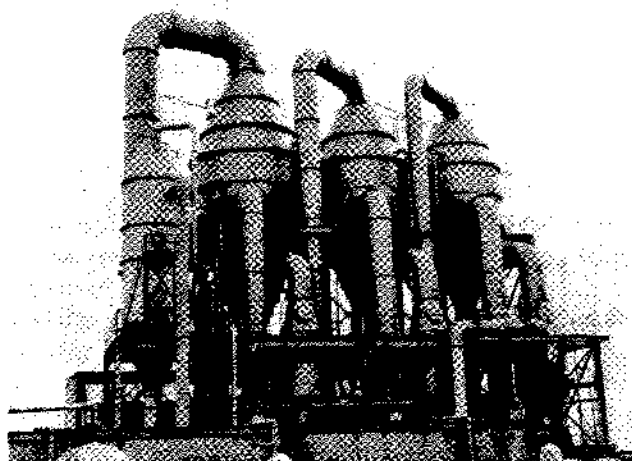


Figure 5. Triple effect evaporating crystallizer.

TABLE 3

Typical Analysis of Product Salt

Chemical Analysis	Common Grade Salt	High Grade Salt
NaCl	96.58%	99.32%
Moisture	2.40%	0.22%
Others	1.02%	0.46%
CaSO ₄	0.14%	0.06%
MgCl ₂ ·6H ₂ O	0.47%	0.22%
CaCl ₂ ·6H ₂ O	0.12%	0.07%
KCl	0.29%	0.11%

Steam and power generation. The salt manufacturing process by electrodialysis utilizes two types of energy. Electricity is used mainly for electrodialysis and steam is used mainly for evaporating crystallization. Therefore, a combination of steam and power generation is effective for the process. High pressure steam produced by a boiler generates electric power in a turbine and exhausted steam from the generator is utilized in evaporating crystallization.

Performance of the process. Based on the actual performance in salt manufacturing plants, the expected performance of salt manufacturing plants using electrodialysis is summarized in the following figure and tables. Three different capacities are chosen at 50,000, 100,000 and 150,000 metric tons per year. Figure 6 and Table 4 show the material and utility balance of the process and Table 5 shows its unit consumption of seawater, electricity, steam and chemicals.

Other applications. The electrodialysis process is a unique technology to produce salt from seawater. The

technology completely modernized the salt manufacturing process in Japan. At present, the ion-exchange membrane technology developed by Asahi Chemical covers not only the salt manufacturing but also various following applications: 1) Brackish or seawater desalination, 2) City sewage desalination (water reuse), 3) Whey desalination, 4) Nickel recovery in plating process, 5) Caustic soda production, 6) Adiponitrile (Nylon 6.6 intermediate) production, and 7) Uranium reduction.

The details of these applications are not described in this paper. They are well-established technologies. The authors believe that the ion-exchange membrane technology will be utilized in different fields as well as in salt manufacturing.

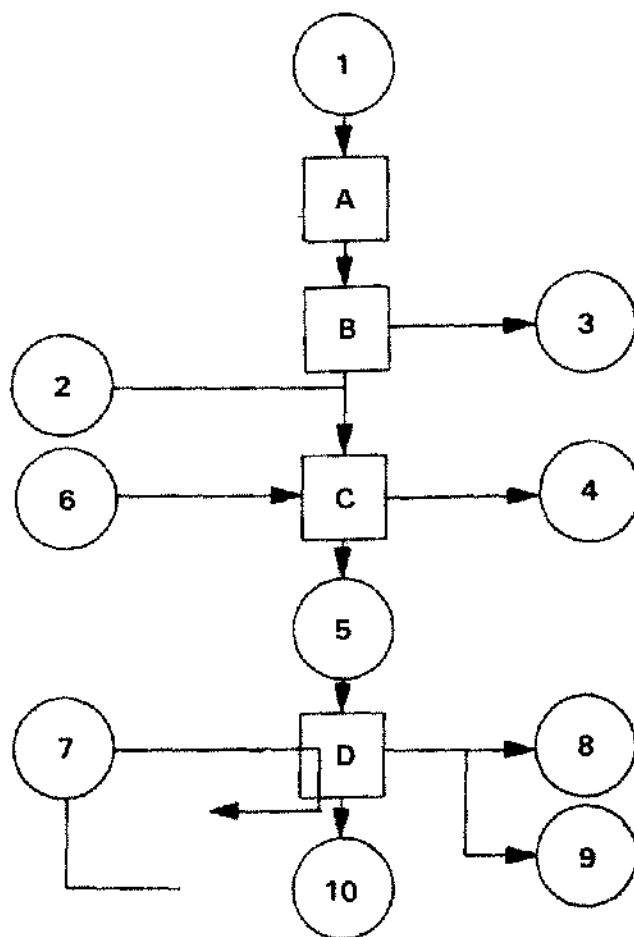


Figure 6. Material and utility balance. 1, For whole plant. 2, Filtered seawater. 3, Backwash disposal. 4, Desalinated seawater. 5, Produced concentrated brine. 6, Electric power. 7, Live stream. 8, Condensate water. 9, Bittern. 10, NaCl (dry base). A, Seawater intake. B, Seawater filter. C, Electrodialyzers. D, Evaporating crystallizers.

TABLE 4
Material and Utility Balance List

	50,000	MTA	100,000	MTA	150,000	MTA
1 Seawater for whole plant (Cl ⁻ = 0.5N)	1,100	m ³ /H	2,000	m ³ /H	3,000	m ³ /H
2 Filtered seawater	960	m ³ /H	1,730	m ³ /H	2,500	m ³ /H
3 Backwash disposal	140	m ³ /H	270	m ³ /H	500	m ³ /H
4 Desalinated seawater (Cl ⁻ = 0.37 N)	918	m ³ /H	1,654	m ³ /H	2,382	m ³ /H
5 Produced concentrated brine	42	m ³ /H	75.9	m ³ /H	118	m ³ /H
6 Electric power	2,640	KW	4,760	KW	6,950	KW
7 Live steam	21	T/H	26.3	T/H	38.5	T/H
8 Condensate water	19.5	T/H	46.7	T/H	72.7	T/H
9 Bittern	1.8	T/H	3.3	T/H	6.1	T/H
10 NaCl (Dry base)	7.0	T/H	12.7	T/H	18.9	T/H

TABLE 5
The List of Unit Consumption

Annual Production Capacity	50,000	MTA	100,000	MTA	150,000	MTA
Seawater (m ³ /T-Salt) for Electrodialyzer	137		137		137	
Electric power (KWH/T-Salt)						
for Electrodialyzer	280		280		280	
for Pumps	52		50		47	
for Evaporating Crystallization	48		45		42	
for Packing	10		10		10	
Average cap. for whole plant	2,640 ^{KW}		4,760 ^{KW}		6,950 ^{KW}	
Steam (T/T-Salt)	3.0		2.1		2.1	
Maximum boiler cap.	22 T/H		30.8 T/H		43.5 T/H	
Chemicals						
35% HCL for cathode rinse stream of electrodialyzer	2.5 kg/T-Salt (430 kg/D)		2.5 kg/T-Salt (760 kg/D)		2.5 kg/T-Salt (1,134 kg/D)	
Antiform agent for evaporating crystallizer	0.07 L/T-Salt (12 L/D)		0.06 L/T-Salt (18 L/D)		0.06 L/T-Salt (27 L/D)	

APPENDIX

History of the Development of
Ion-Exchange Membrane and its
Applications by Asahi Chemical
Industry Co., Ltd.

SALT

- 1950 Start of the fundamental study of ion exchange membrane and its applications
- 1953 Establishment of the production technology of homogeneous ion exchange membrane (CK-1 and CA-1 type)
- 1956 Start of the test electrodialyzer operation (Membrane size: 60 cm × 60 cm). Start of the membrane production at Nobeoka pilot plant (Membrane size: 1 m × 1 m)
- 1957 Start of the test operation of the commercial size electrodialyzer (Membrane size: 1 m × 1 m). Start of the pilot plant operation of vapor compression type crystallizer with external heater and forcing recirculation
- 1960 Start of the commercial membrane production at Kawasaki plant
- 1961 Start of the commercial operation of Onahama Salt Factory (Table salt: 50,000 T/Y)
- 1964 Start of the production of the new type anion exchange membrane (CA-2 type)
- 1965 Start of the production of uni-valent permselective ion exchange membrane (CK-2 type: Cation exchange, CA-3 type: Anion exchange)
- 1967 Start of the commercial operation of Akoh Salt Factory (Table salt: 33,000 T/Y). Start of the commercial operation of Naruto Salt Factory (Table salt: 13,000 T/Y)
- 1969 Start of the commercial operation of Naruto Salt Factory (Table salt: 20,000 T/Y)
- 1970 Start of the production of reinforced membrane (K-101, A-101, K-102 and A-102 type)
- 1973 Total capacity of the salt factories using Asahi Chemical's technology after the expansion
- | | |
|----------------------|-------------|
| Onahama Salt Factory | 190,000 T/Y |
| Akoh Salt Factory | 184,000 T/Y |
| Naruto Salt Factory | 181,000 T/Y |
| Naikai Salt Factory | 20,000 T/Y |
| Total | 575,000 T/Y |
- This capacity is nearly half of the total capacity of the salt production in Japan.
- 1975 Start of the commercial operation of TESF (Table salt: 110,000 T/Y)

- 1977 Conclusion of the contract with Petrochemical Service Center Co., Ltd. in Korea concerning the export of salt manufacturing plant by use of ion exchange membrane. It is now under construction as of Feb., 1978. (Table salt: 150,000 T/Y)

OTHERS

- 1961 Start of the operation of the brackish water desalination plant at Webster, U.S.A. (Tap water: 950 M³/D). Start of the operation of the uranium reduction unit at Japan Atomic Fuel Corporation (4.2 kg/H)
- 1967 Start of the test operation of the Adiponitrile pilot plant
- 1968 Start of the developmental study of the chloralkali process using ion exchange membrane. Start of the commercial operation of Central Glass plant (Salt: 10,000 T/Y)
- 1970 Start of the operation of the Shikine-jima brackish water desalination plant (Tap water: 20 M³/D)
- 1971 Start of the commercial operation of Adiponitrile production plant (25,000 T/Y)
- 1972 Start of the production of the anion exchange membrane which is resistant to organic fouling (A-201 type). Start of the operation of the larger commercial size electrodialyzer (Membrane size: 1.3 m × 1.3 m)
- 1972 Start of the operation of the 1st Oshima brackish water desalination plant (Tap water: 1,000 M³/D). Start of the operation of the brackish water desalination plant at Brindisi, Italy (1,200 M³/D). Start of the operation of the Minamisuna pilot plant. (Feed: Treated city sewage, Capacity: 250 M³/D). Start of the operation of the pilot uranium reduction plant at Ningyo-toge (100 T/Y)
- 1973 Start of the pilot plant operation of the chloralkali process using ion exchange membrane (4,400 T/Y)
- 1974 Start of the operation of the 2nd Oshima brackish water desalination plant (Tap water: 1,000 M³/D). Start of the operation of the Noshima seawater desalination plant (Tap water: 120 M³/D). Start of the operation of the Ni recovery unit (2 units, 450 kg/M each)
- 1975 Start of the commercial plant operation of the chlor-alkali process using ion exchange membrane (Caustic soda 40,000 T/Y). Start of the operation of the whey desalination plant
- 1976 Start of the commercial operation of the Denki Kagaku Plant using ion exchange membrane (Caustic soda: 60,000 T/Y). Start of the operation of the whey desalination plant in West Germany
- 1977 Conclusion of the contract with Prince Albert Pulp Company, Ltd. in Canada concerning the export of ion exchange membrane chlor-alkali plant. (Caustic soda: 30,000 T/Y)