Concentration of Seawater by New Electrodialysis Process

T. Kawahara, K. Suzuki and K. Asada
Asahi Glass Co., Ltd.
Tokyo, Japan

ABSTRACT

A new electrodialysis process including new ion exchange membranes and electrodialyzer was developed by Asahi Glass Co., Ltd. and two commercial plants with capacities of 170,000 (t-NaCl/Year) are in operation for the production of table salt from seawater. It has, as its main features, low energy consumption, high concentration and purity of brine, and easy and stable operation, compared with the conventional process. Therefore, the electrodialytic concentration process appears more attractive than has been the case, not only table salt but also for industrial use.

INTRODUCTION

Japan's electrodialysis technique is now among the best in the world and it is used in the field of seawater concentration, brackish water desalination, purification of pharmaceuticals and foodstuffs, reuse of waste water and various electrolysis processes.

All table salt in Japan has been produced by the electrodialysis seawater concentration technique for the last ten years, and there are 7 salt factories using 3 different processes. Among the 3 membrane-supplying companies, Asahi Glass, the leading company in the soda industry and the largest consumer of industrial grade salt in Japan, has been developing the electrodialysis process for a quarter century through its own research and development activities for the self-supply of raw salt in its chlorine-alkali factories.

Around ten years ago, Asahi Glass developed a combination process of the electrodialysis and the electrolysis techniques for the utilization of waste seawater from a desalination plant by participation in the National Big Project "Seawater Desalination and Re-utilization of By-product" sponsored by the Government.

After the completion of that project, Asahi Glass developed an improved electrodialysis, mainly for the reduction of energy consumption and the improvement of operation and construction costs. This new process was commercialized in 1980 as the replacement for the existing conventional plant, and Asahi Glass now has over two years' experience with the new process through construction and operation of commercial plants in Naikai Salt and Sakito Salt Manufacturing. Asahi was granted the Honour of the Great Prize for the commercialization of this new process from the Japan Seawater Science Society in 1982.

Asahi Glass's new electrodialysis process has, as main features, low energy consumption, a high concentration and high brine purity, and easy and stable operation, compared with the existing conventional process.

PROGRESS OF TECHNICAL DEVELOPMENT WORK BY ASAHI GLASS

Asahi Glass began research and development work on the ion exchange membrane "Selemion" in 1950. After numerous variations in subsequent years, the styrene-divinyl benzene polymerized membrane has been developed and is in current use. Electrodialyzers were also developed at the same time, and many practical electrodialyzers have been developed for concentration and desalination.

The course of development of Selemion membranes and the electrodialyzers and the state of practical use for seawater concentration and large-scale desalination are shown in Table 1. The history of their application and development can be divided into four stages.

Ion Exchange Membrane

In the membrane manufacturing plant constructed in 1960, SBR (styrene-butadiene rubber) membrane reinforced by glass fibre were produced on an industrial scale. About 1965, styrene-divinyl benzene-copolymerized membranes reinforced with synthetic fibre began to be manufactured. These membranes were adopted for practical use for plants supplied to Naikai Salt Manufacturing Co.

TABLE 1

Progress of Technical Development Work

Years	Ion-exchange Membrane	Electrodialyzer	Pilot and Commercial Plant
	• Start of research and development ↓		
1950S	Development of SBR-Membrane ↓ Improvement of SBR-Membrane ↓	Development of unit cell type electrodialyzer ↓	• Underground brine concentration test (— '61) ↓
	• Construction of membrane manufacturing plant in Kansai Factory ↓		• Seawater concentration plant in Kitakyushu (2,500 t/Y) ↓
1960S	Improvement of SBR-Membrane ↓ • Development of ST-DVB-Membrane ↓	• (Development of Model DU, CU electrodialyzer) ↓	• Seawater concentration plant in Kitakyushu (10,000 t/Y) and Nihon Chemicals and Salt Manufacturing (10,000 t/Y) ↓
	• Construction of membrane manufacturing plant in Chiba Factory	• Development of Model CB-V electrodialyzer ↓	• "National Big Project" ↓ Commercial plant in Naikai and Sakito (150,000 t/Y) ↓
		• (Development of Model DW electrodialyzer) ↓	
1970S		• (Development of Model DS electrodialyzer) ↓	• (Desalination plant for Tokyo Electric Power (2,000 t/D) and Kashima Minami Joint Electric Power (12,000 t/D)) ↓
	• Development of Selemion CMR, ASR	• Development of Model CS-V electrodialyzer	• Pilot test of new electrodialysis process in Naikai and Sakito ↓
			• New Commercial plant in Naikai (170,000 t/Y) (— '81)
1980S			• New commercial plant in Sakito (170,000 t/Y) (— '82)

and Sakito Salt Manufacturing Co. under the salt industry modernization plan in 1971–1972.

Selemion CMR and ASR, developed in 1978 for the main purpose of energy saving, are presently used by the two above-mentioned companies.

Electrodialyzer

After a comparative study of an underground brine concentration test performed at Oami, Chiba Prefecture, starting in 1957, Asahi Glass adopted the unit cell type for its Kitakyushu works and Nihon Chemicals and Salt Manufacturing Co. The latter operation started in 1961 with a 10,000 ton/year plant. Other desalination electrodialyzers developed at that time were of the filter-press type. On the basis of these experiences, Asahi Glass decided to adopt a filter-press type electrodialyzer for Sakito Salt Manufacturing and Naikai Salt Manufacturing, and developed Model CB-V and supplied it to the companies.

In 1978 Asahi Glass developed an energy-saving electrodialyzer model CS-V, together with new membranes Selemion CMR and ASR. Two users, Naikai and Sakito, replaced all of the conventional electrodialyzers with the new ones in 1980 and 1981.

Electrodialyzers for seawater concentration are required to meet the following conditions: Low electric power consumption, high salt content in concentrated brine, high production capacity per unit, and easy and long-term stable operation. Accordingly, the following are desired in design.

- The distance between membranes should be made as small as possible
- The spacer and the distribution mechanism should be such that the flow of seawater may be even, and the circulation pressure loss may be minimal
- Ease of assembly and handling
- A high limiting current density, and no scale formation.

SPECIAL FEATURES OF THE ELECTRODIALYSIS PROCESS

This process is a quite efficient table salt production method as a substitute for the conventional solar salt field method. It consists of an electrodialysis seawater concentration process and vacuum type multieffect evaporating crystallization process. Furthermore, seawater intake facilities and drying and packing equipment for solid salt are installed in the plant.

In these techniques, the evaporating crystallization and drying and packing sections are fundamentally the same as those of the conventional solar salt field method. So the conventional technique is applicable in the electrodialysis process by minor improvement.

Special features of the electrodialysis process may be compared with the solar salt field process for Japanese domestic conditions. The solar salt field technique is similar to the agricultural method but the electrodialysis process is quite industrial. The special features of the electrodialysis process are shown in Table 2.

Because the electrodialysis process concentrates seawater by electric energy, a stable supply of electrical energy is required and a better quality seawater having lower contamination than with the solar salt field method is necessary. Thus caution should be exercised in the selection of plant site condition and specifications of seawater intake facilities.

Because brine quality substantially influences the performance of the crystallization section, a high quality electrodialysis brine enables easy operation and maintenance of the crystallization section. Accordingly, long-term stable operation and a high quality product are expected.

TABLE 2

Features of Electrodialysis Process

	Electrodialysis Process	Salt Field Method
Required Land Area	Narrow (Approx. 1/60 of salt field)	Wide
Operator	Few (Approx. 1/10 of salt field)	Many
Concentration of Produced Brine	High (Approx. 35% more than salt field brine)	Low
Purity of Produced Brine	High (Approx. 40% Higher than salt field brine)	Low
Operation	Automatically operated	Automatic operation is difficult
Load Factor	Operation is not influenced by weather	Operation is influenced by weather

PROCESS DESCRIPTION OF TABLE SALT MANUFACTURING

This process is basically composed of the electrodialysis seawater concentration process and the evaporating crystallization process. First, seawater is concentrated in the electrodialyzer to produce concentrated brine of about 20%. The brine exhausted from the electrodialyzer is directly evaporated and crystallized by means of multi-effect vacuum type evaporators. The salt manufacturing process is shown in Figure 1 while Figure 2 shows its process flow sheet.

Electrodialysis Process

Prior to its use in the electrodialysis section, seawater is employed as a coolant in the barometric condenser of the crystallization section to recover waste heat and cause a temperature rise of the seawater. In the electrodialysis section, seawater is received in a seawater pit and then filtered by means of an automatic, backwash gravity sandfilter to remove suspended solids to the desired level. Filtered seawater is fed to the electrodialyzers, and by the application of DC electricity, the dissolved salt in seawater (mainly sodium chloride) is permeated through ion-exchange membranes and is concentrated to produce the brine. After a single pass of the dilute stream through the electrodialyzers, the main part of waste seawater is discharged to the waste stream, while a part is reused as the anode rinse liquor. The cathode rinse liquor, which is a dilute hydrochloric acid solution, is recycled separately.

In the concentrate chamber of the electrodialyzer, brine is recycled so as to balance the hydraulic pressure of the dilute chamber and the concentrate chamber. An increased amount of the brine produced by electrodialytic concentration is overflowed from the brine pit to the brine storage pit. The brine in the storage pit may be used in the crystallization section directly. Although a univalent ion permselective technique is applied a small amount of hydrochloric acid is dosed into the concentrate stream for the prevention of scale formation in the concentrate chamber. Long term stable operation with high univalent permselectivity is ensured without any complicated operation and maintenance work.

DC electricity for electrodialysis is supplied from the rectifier installed in this plant after receiving high tension AC electricity inside the battery limits of the plant. For the security of the plant, a simple automatic operation system with an interlock circuit is installed in the plant and automatic operation is performed in the usual condition.

Crystallization Process

There are three stages of vacuum type evaporator in the crystallization section and the brine is first fed to the third evaporator to concentrate it to a somewhat lower concentration than saturation. The main part of extracted liquor

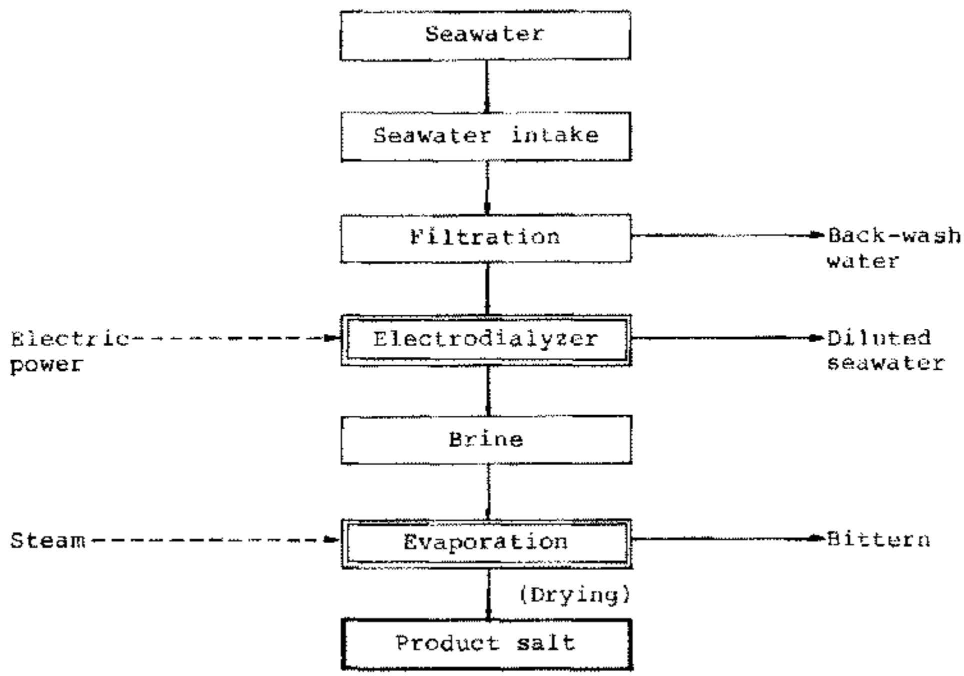


Figure 1. Salt Manufacturing Process

from the 3rd. evaporator is fed to the 1st. evaporator and crystallized to solid salt, while mother liquor is extracted and continuously fed to the second evaporator. In each evaporator of the outside heating system, brine is recycled between the evaporator and heating equipment. The slurry of solid salt and mother liquor from the first and second evaporators are extracted from the bottom, and solid salt is separated by means of a slurry tank and centrifugal separator. Fine crystal salt is floated from the slurry tank and recycled to the second evaporator together with a part of extracted brine from the first evaporator.

Heating of liquor in the evaporator is done in the following manner. Steam is first fed to the heater of the first evaporator and exhausted condensate is recycled to the boiler through the heat exchanger. The second evaporator is heated by generated vapor from the first evaporator and the third evaporator is heated by generated vapor from the second evaporator. The steam generated in the third evaporator is condensed in a barometric condenser to create a vacuum condition in the third evaporator. Exhausted condensate from heaters of the second and third evaporators are passed through heat exchangers to recover waste heat to the liquor. Forced recycling of liquor between heater and evaporator raises the efficiency of heat transfer in the heater and prevents the formation of scale on the surface of the heating tubes or inner walls of the evaporators and piping.

The above mentioned flow pattern of the brine and liquor enables a good distribution in the crystal size of salt.

NEW ELECTRODIALYSIS PROCESS FOR CONCENTRATION OF SEAWATER

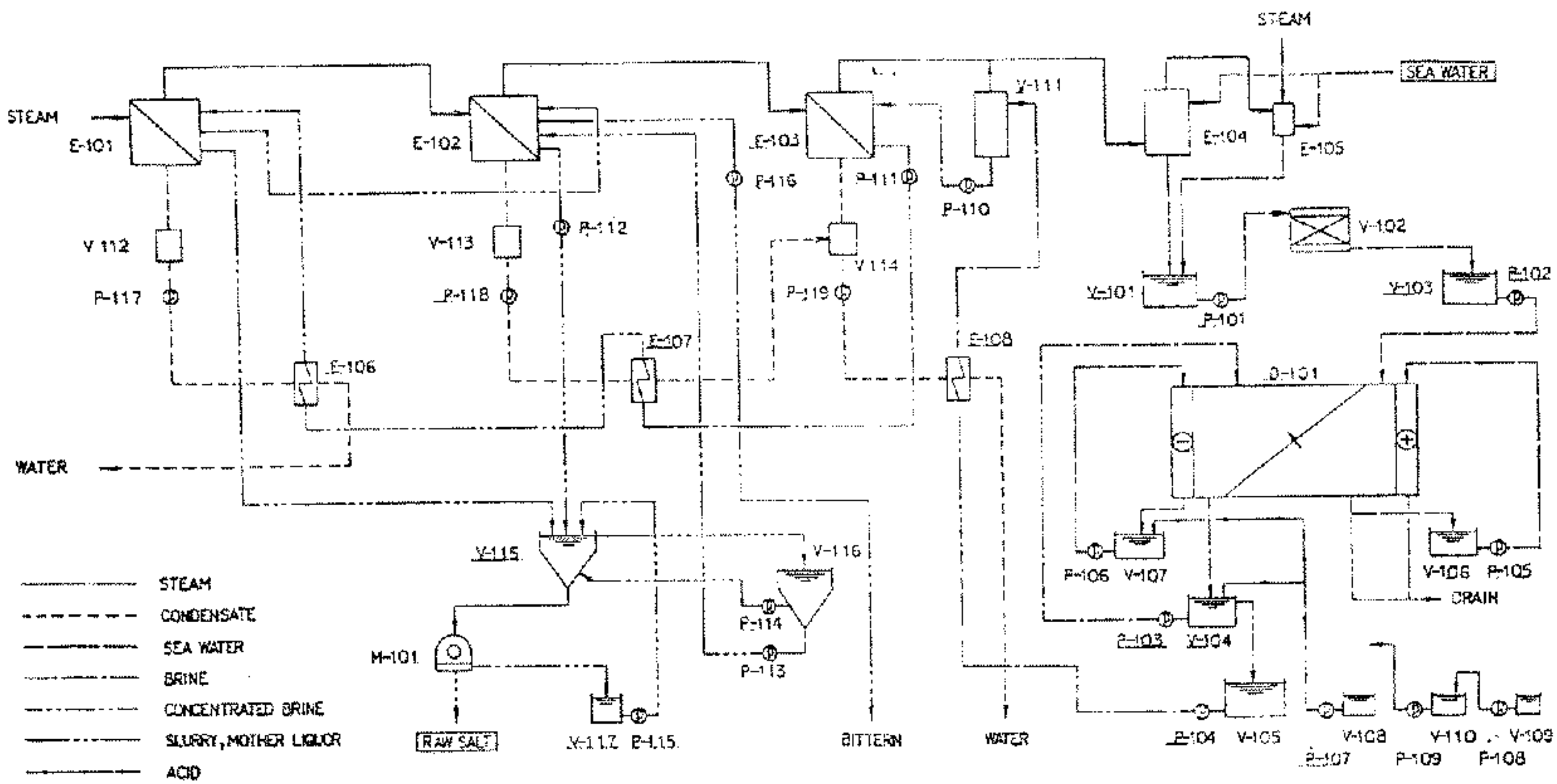
Progress of Development

Establishment of an energy-saving seawater concentration process was long desired in order to reduce salt manufacturing costs against the background of soaring oil prices after the first oil crisis.

Under the circumstances, Asahi Glass continued technical development with a view to reducing the usual concentration electricity consumption 300–320 kwh/t NaCl by more than 30%, and to raising the brine concentration of NaCl 160–170 g/l by more than 30%, particularly with respect to ion exchange membranes, electrodialyzers and process technique.

As a result, Asahi Glass obtained a prospect for success in developing the new electrodialysis process, manufactured new membranes and electrodialyzers on a trial basis and conducted tests on them for their practical utilization. Asahi delivered its first units to two companies early in 1979 for test operation.

As a result of the trials, Naikai Salt Manufacturing Co. decided to replace all of its electrodialyzers with new ones. They have been in operation since August 1980, produc-



ITEM NO.	NAME	ITEM NO.	NAME	ITEM NO.	NAME	ITEM NO.	NAME
E-101~103	EVAPORATOR (CRYSTALLIZER)	V-108	ACID TANK	P-104	BRINE FEED PUMP	P-115	TAIL PUMP
E-104	BAROMETRIC CONDENSER	V-109	CHEMICALS TANK	P-105	ANODE RINSE PUMP	P-116	BITTERN PUMP
E-105	EJECTOR SYSTEM	V-110	CHEMICAL CLEANING TANK	P-106	CATHODE RINSE PUMP	P-117	CONDENSATE FEEDBACK PUMP
E-106~108	BRINE PREHEATER	V-111	DECARBONATER	P-107	ACID PUMP	P-118~119	CONDENSATE PUMP
V-101	SEA WATER PIT	V-112~114	CONDENSATE FLASH TANK	P-108	CHEMICALS PUMP	D-101	ELECTRODIALYZER
V-102	SAND FILTER	V-115	SLURRY TANK	P-109	CHEMICAL CLEANING PUMP	M-101	CENTRIFUGE
V-103	FILTERED SEA WATER PIT	V-116	MOTHER LIQUOR TANK	P-110	EVAPORATOR FEED PUMP		
V-104	BRINE PIT	V-117	TAIL TANK	P-111	CRYSTALLIZER FEED PUMP		
V-105	BRINE STORAGE PIT	P-101	SAND FILTER FEED PUMP	P-112	SLURRY PUMP		
V-106	ANODE RINSE PIT	P-102	DILUTE PUMP	P-113	MOTHER LIQUOR FEED PUMP		
V-107	CATHODE RINSE TANK	P-103	CONCENTRATE PUMP	P-114	MOTHER LIQUOR PUMP		

Figure 2. Process Flow Sheet

ing excellent operating results. Sakito Salt Manufacturing Co. also introduced the new electrodialysis process in April, 1981.

Special Features of New Process

Asahi Glass's new electrodialysis process has several special features compared with the existing conventional process.

- Largest production capacity—Largest size of ion-exchange membrane of over 2 m^2/sheet and large number of approximately 1500 pairs or more of membranes installed in a unit enables annual production of around 12,000 tons or more of salt in one unit of the electrodialyzers
- Low energy consumption—Special design improvements of the membrane and the electrodialyzer decreases electricity consumption in the electrodialysis process. Further, high sodium chloride content in the brine decreases steam consumption in the crystallization process
- Simplicity of the plant and high utilization of seawater—Special inner design of the electrodialyzer enables high recovery of salt from seawater by the single-stage and single-pass system of seawater in the dilute chamber. So, there is no need to recycle seawater in the unit and, accordingly, plant design is substantially simplified
- Easy to operate—Because the plant design is simple, operation of the electrodialyzer is done by a few persons using simple automatically controlled systems
- Simplicity of maintenance and long term stable operation—The electrodialyzer is operated for long periods without contamination inside the unit because of a specially designed process technique.

Frequency of the maintenance or cleaning of the electrodialyzer is once a year or less and, accordingly, the replacement rate of the membrane is lower than that of the conventional method.

COMPARISON OF NEW PROCESS WITH THE CONVENTIONAL TYPE

A comparison of the new process with the conventional type is shown in Table 3.

The following benefits could be realized as a result of development of the electrodialysis process:

1. Concentration of NaCl in brine is increased about 35(%)
2. Brine purity is increased from 89(%) (NaCl/T.salts) to 95(%)
3. Electric power consumption is reduced about 35(%)
4. Production capacity is increased about 27(%)
5. Operation and maintenance are easy. Long, stable operation over a year is expected and membrane replacement is reduced.

TABLE 3

Comparison of New Process with the Conventional Type

Item	New	Conventional
1. Specifications of electrodialyzer		
Designation	Model CS-V	Model CB-V
Ion-exchange membrane	Selemion CMR and ASR	Selemion CMV and ASV
Size of membrane (cm × cm)	112 × 230	112 × 200
Number of cell pairs (Pairs/stack)	250	75
Number of stacks (Stacks/block)	6	18
Total number of cell pairs (Pairs/block)	1,500	1,350
2. Standard operating conditions		
Electric current (A)	630	630
Flow rate of seawater (m^3/hour.block)	186	394
Temperature (°C)	25	25
Concentration of seawater (CL^--N)	0.52	0.52
3. Performance data		
Concentration of NaCl in brine (g/l)	230	170
Brine purity (%) (NaCl/T.salts)	95	89
Power consumption (KWH/ton.NaCl)		
Electrodialysis	225	320
Pumps	32	52
4. Production capacity (NaCl-tons/day.block)	42	33
5. Scheduled maintenance	Once a year	Every 3 months
6. Membrane replacement (%/year)	<5	10

Operation Results

The performance data of a commercial plant that was put into operation by Naikai Salt Manufacturing late in August 1980 is shown in Figure 3. The new plant demonstrates higher performance than the originally designed performance in all respects.

Figure 4 presents a photo of the new electrodialyzer and its exterior view is shown in Figure 5. Figure 6 illustrates an isoenergetic curve prepared by the Japan Tobacco & Salt Public Corporation. It is assumed that 2.6 tons of water can be evaporated with 1 ton of steam, with the use of triple-effect evaporators, and that the electric power unit price is ¥17.6/kwh, the heavy fuel unit price ¥58.4/l, and heavy fuel consumption 70 ℓ per ton of generated steam.

In Figure 6, the energy cost in the case of the conven-

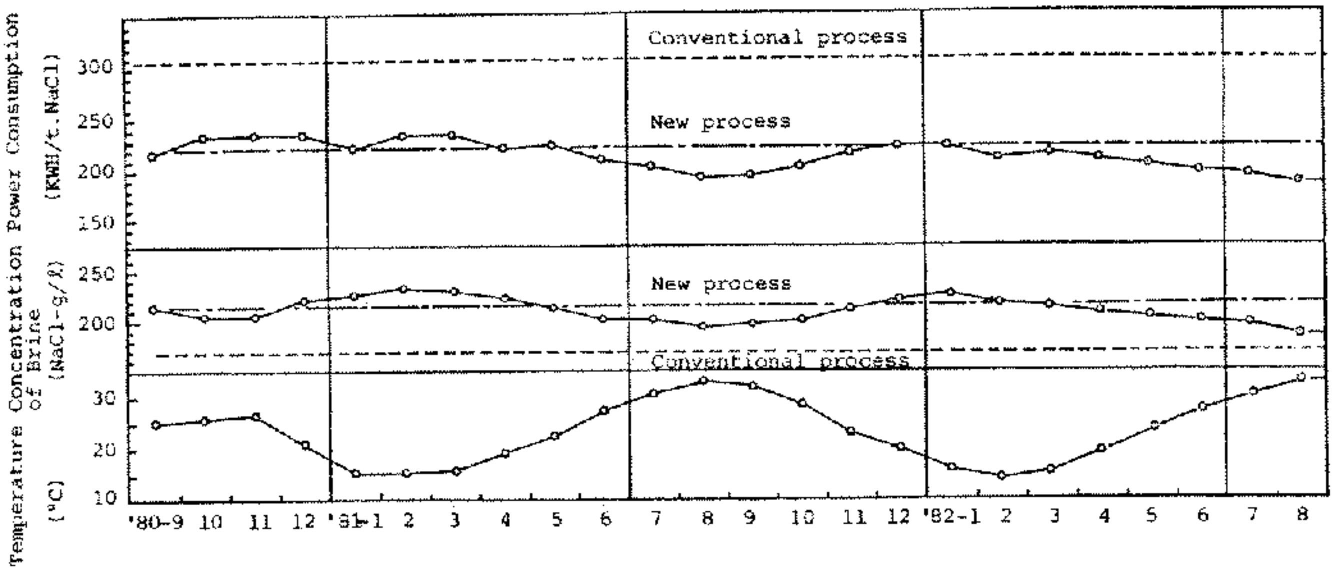
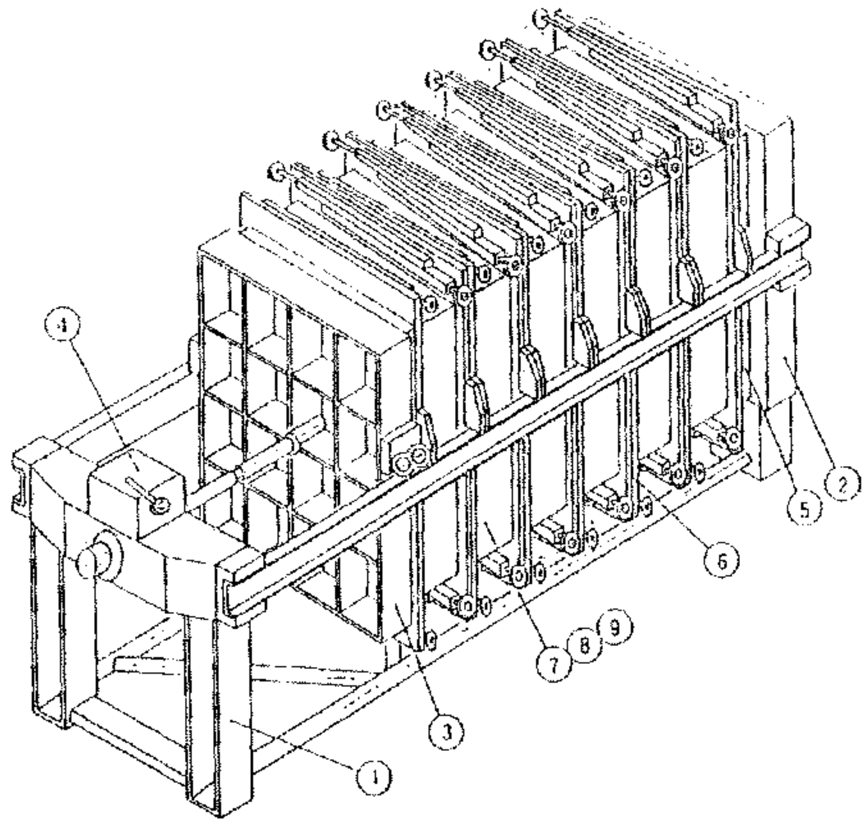


Figure 3. Performance data of the commercial plant

Figure 4. Photograph of new electrodialyzer Model CS-V



1	Fastening Frame
2	Fast Head
3	Loose Head
4	Oil Pressure Chamber
5	Electrode Chamber
6	Intermediate Frame
7	Diluate Cell
8	Concentrate Cell
9	Ion Exchange Membrane

Figure 5. Model CS-V Electrodialyzer

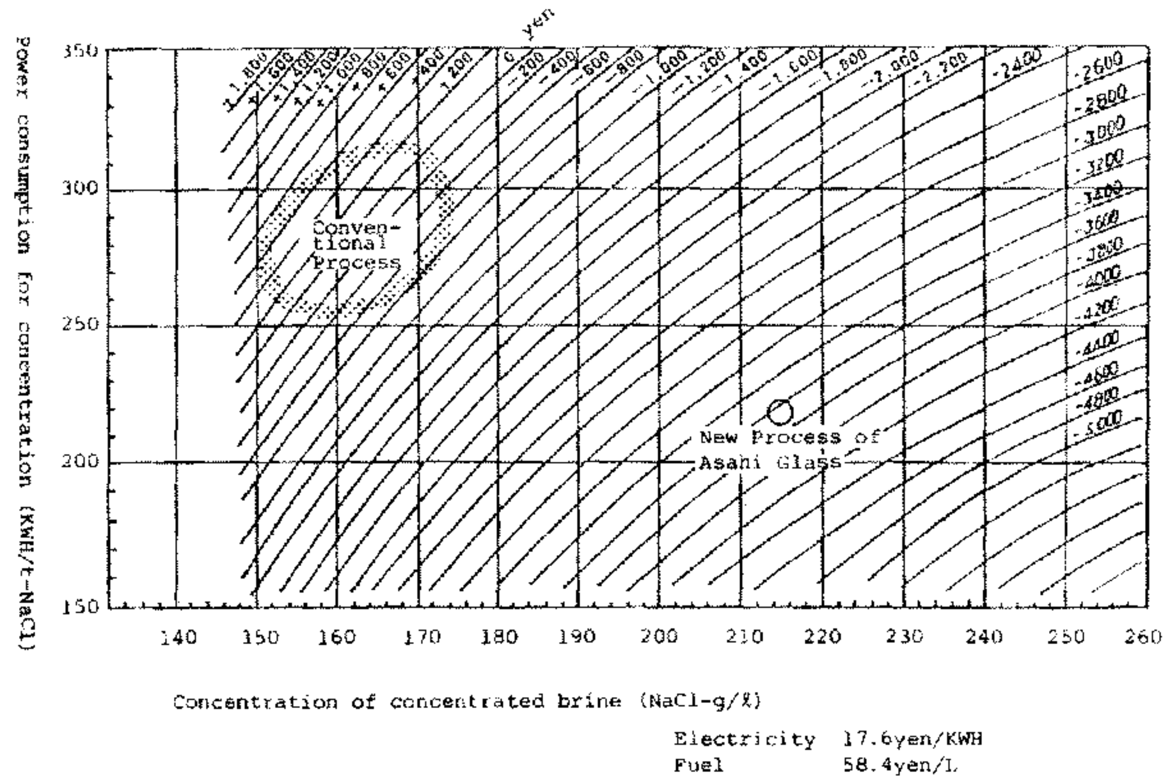


Figure 6. Comparison of energy cost in electrodialysis process

tional process is assumed to be 0, and energy cost changes due to changes in specific electric power consumption and brine salt concentration are expressed by + or −. In the conventional process, energy costs are equal when brine salt concentration is 160 g/l and electric power consumption is 275 kwh/t, and when the concentration is 170 g/l and the power consumption is 315 kwh/t. As the standards of the conventional process, these are the basis for comparison.

It is to be understood that the energy cost is lower than that with the conventional process by ¥4,000/t. Considering that the present common salt price is ¥22,600/t, this is a process leading to drastic rationalization. As heavy fuel oil prices rise more, cost can be saved in comparison with the conventional process.

UTILIZATION OF WASTE SEAWATER FROM THE DESALINATION PLANT

Seawater desalination plants discharge a huge quantity of waste concentrated seawater. Because the seawater from the flash evaporator, for example, contains twice as much salt as the original seawater and its temperature is maintained constantly at high temperature throughout the year, the concentration process is more efficient than the ordinary seawater concentration process in electrodialysis.

As a result, research and development efforts were made in the National Big Project "Seawater Desalination and Reutilization of Byproduct," sponsored by the Government, in order to recover the useful by-products from the waste concentrated seawater produced by the evaporator. Asahi Glass undertook research and development of the diaphragm type electrolysis process following the reconcentration of the waste concentrated seawater by the perience, is substantially reduced by the new electrodialysis process.

Concentration of brine, cell pair voltage and electric power consumption in both cases of utilizing waste concentrated seawater and raw seawater are shown in Figures 8, 9 and 10, respectively. In the case of utilizing raw seawater, maximum current density is about 4 (A/dm^2) in order to prevent pH change of dilute. On the contrary, higher current density can be applied in the case of utilizing waste concentrated seawater owing to high temperature and concentration.

Table 4 shows a most remarkable comparison of performance data.

For the same production capacity, the electrodialysis equipment is decreased to almost 50% of required membrane area. Further, NaCl content in the brine is increased remarkably.

By the experience of the prototype unit in the "National Big Project," raw seawater and waste concentrated sea-

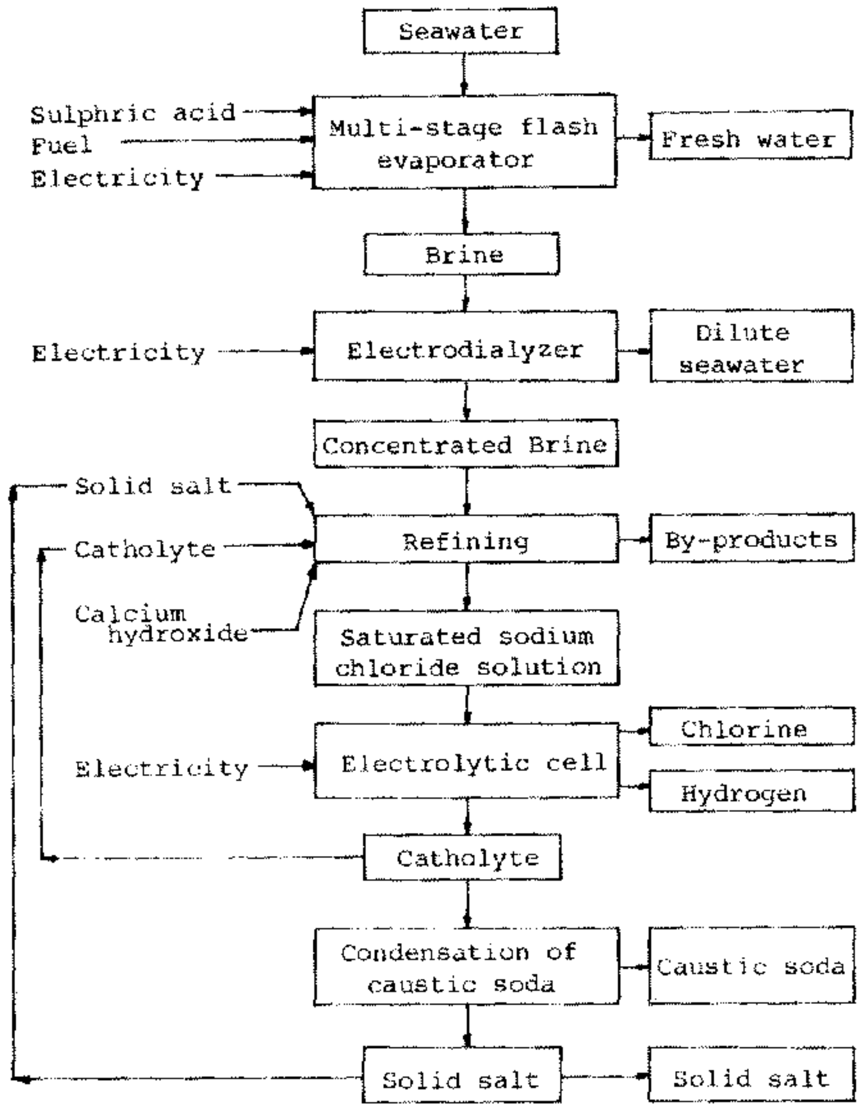
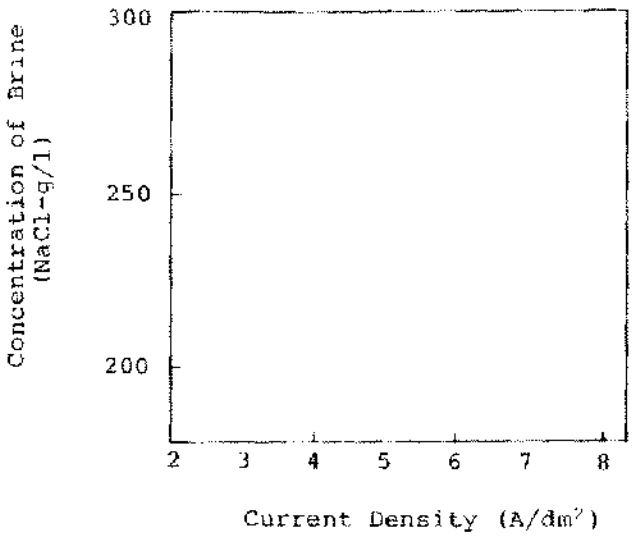


Figure 7. Flow sheet for full utilization of seawater

TABLE 4

Comparison of Performance Data

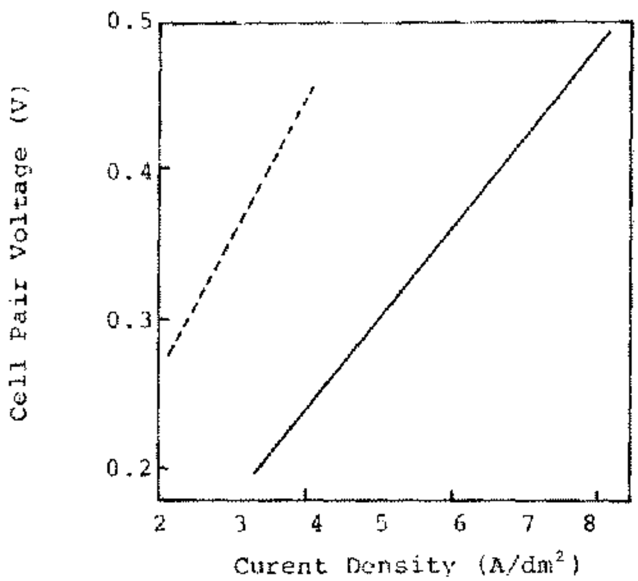
Raw water	Raw seawater	Waste concentrated seawater
Standard current density (A/dm^2)	3.5	7.0
NaCl content in brine (g/l)	230	261
Power consumption (KWH/t.NaCl)	225 ~ 240	225 ~ 240



In the case of waste concentrated seawater (35°C, Cl^- 1.0 N)

In the case of raw seawater (25°C, Cl^- 0.52 N)

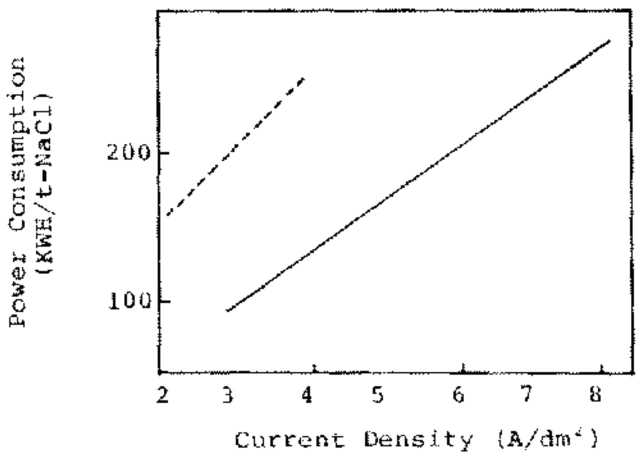
Figure 8. Relationship between current density and concentration of brine



—— In the case of waste concentrated seawater (35°C, Cl^- 1.0 N)

- - - In the case of seawater (25°C, Cl^- 0.52 N)

Figure 9. Relationship between current density and cell pair voltage



—— In the case of waste concentrated seawater (35°C, Cl^-1.0 N)

--- In the case of raw seawater (25°C, Cl^-0.52 N)

Figure 10. Relationship between current density and power consumption

TABLE 5

Design Basis of Concentration

	Filterated waste brine	100,000 (m^3/day) Cl^- 39.4 (g/l)
Balance of waste brine	Concentrated brine	6,930 (m^3/day) Cl^- 169 (g/l)
	Diluated brine	93,070 (m^3/day) Cl^- 29.8 (g/l)
	Current density	7.0 (A/dm^2)
Performance	Purity of brine	96(%) (NaCl/T.salts)
	Power consumption	238 + 32 (KWH/t-NaCl)
	Concentrated brine	2,290,000 (m^3/year)
Production	Table salt	610,000 (t/year)

TABLE 6

Major Specifications of Electrodialysis Plant

	Type	Auto-matic back-wash gravity type
Filter	Diameter	12.5 m
	Filteration velocity	8.5 m/H, 17 m/H (1st stage) (2nd stage)
	Number	6 units
	Type	Model CS-V
	Ion-exchange membrane	Selemion CMR and ASR
Electrodialyzer	Size of membrane	112 cm × 230 cm
	Number of cell pairs	1,500 pairs per block
	Number of electrodialyzers	22 blocks
	Type	Thyrister
Rectifier	Out put	D.C. 700V 1500A
	In put	6.6 KV, 3 Phase, 50 Hz
	Number	22 units

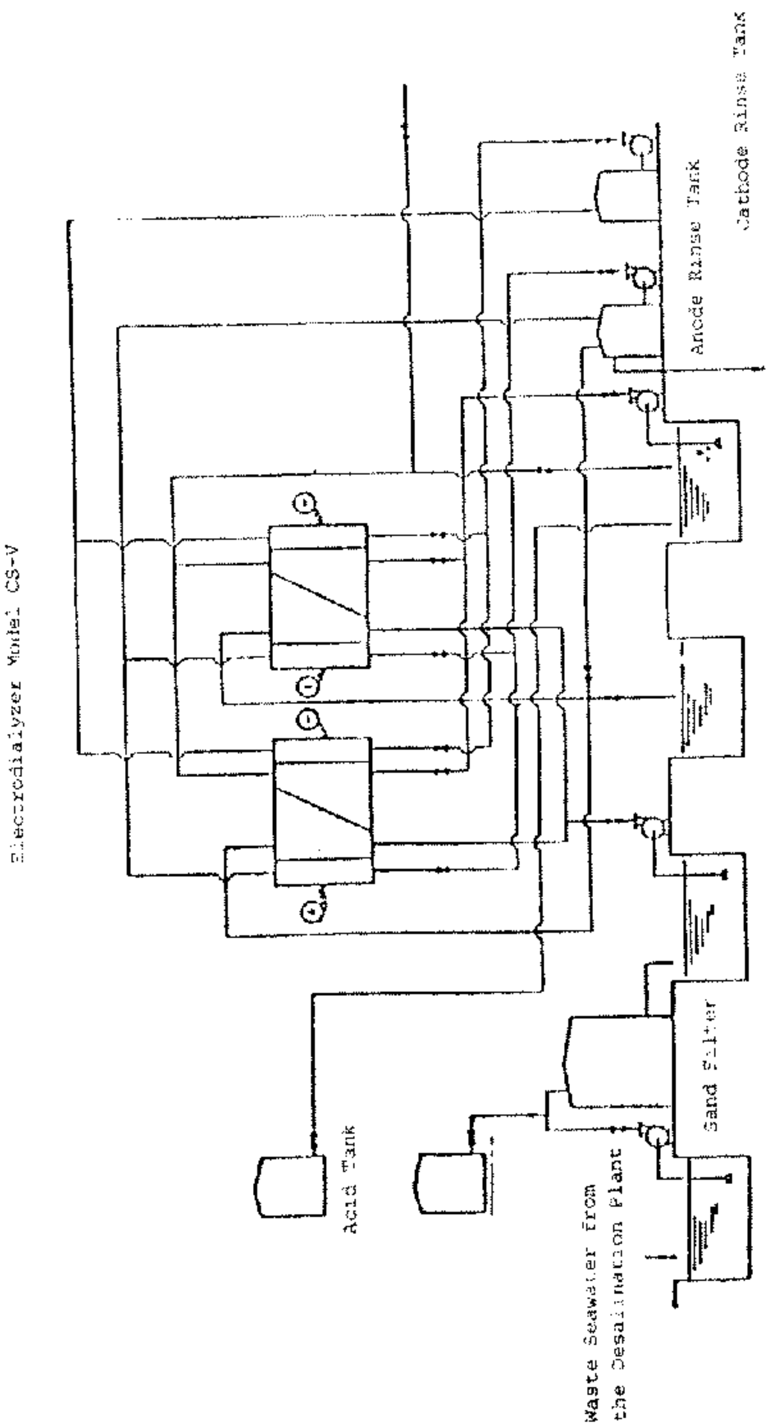


Figure 11. Flow diagram for concentration of waste brine by electrodialysis

Installation cost*	3,388 million yen
Area	7,460 m^2
Personel	12 persons
Electrocity	5 yen/KWH
Cost of salt	2,760 yen/t-NaCl

* All civil works for buildings and foundations are not included.

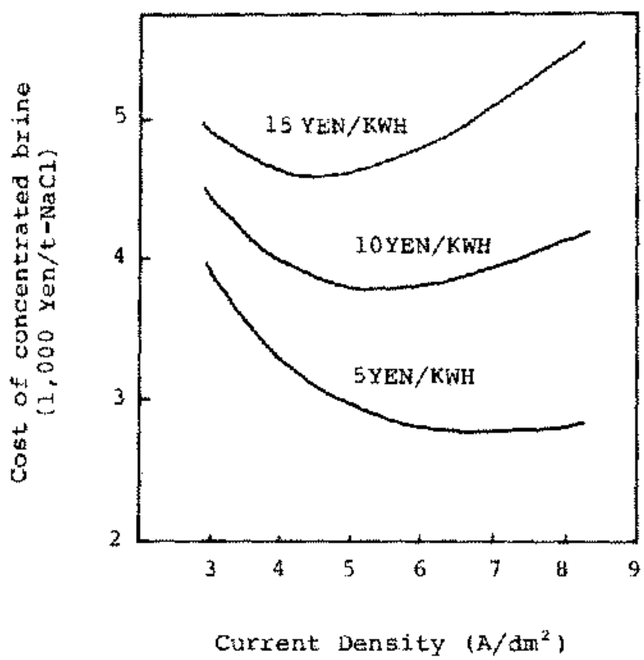


Figure 12. Cost of concentrated brine

electrodialysis process. An outline of the "National Big Project" is shown in Figure 7.

It is expected that the operating cost for recovery of salt, if waste concentrated seawater is utilized based on this ex-water can alternatively be used in the electrodialysis equipment, so long as a rectifier of suitable specifications is installed (T. Hamano, 1975, p. 29). So the electrodialytic concentration of waste brine from a flash evaporator was studied under the design basis shown in Table 5 with the newly developed concentration process.

Table 6 shows major specifications of electrodialysis plant.

Figure 11 shows a flow diagram for concentration of waste brine by the electrodialysis process.

Based on the calculated results of operating conditions and cost estimation for waste brine concentration, installation cost and concentrated brine cost are estimated. The results of cost estimation are shown in Table 7.

The cost of concentrated brine which is substantially reduced is compared with utilization of raw seawater, as shown in Figure 12. The optimum current density was 7(A/dm^2) in the case in which the cost of electricity was 5(YEN/KWH) and decreased with the increasing cost of electricity.

TABLE 7

Results of Cost Estimation

Installation cost*	3,388 million yen
Area	7,460^2
Personel	12 persons
Electrocity	5 yen/KWH
Cost of salt	2,760 yen/t-NaCl

*All civil works for buildings and foundations are not included.

The minimum concentrated brine cost is considered to be competitive with imported salt and makes electrodialytic concentration of waste brine appear economically attractive.

REFERENCES

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