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A New Electrodialyzer Technique for Salt Production by Ion-Exchange Membrane

Ryuji Izuo, Fumio Hanada and Atsushi Tomita

Tokuyama Soda Company Ltd., Tokuyama City, Yamaguchi, Japan

ABSTRACT

Tokuyama Soda has aimed to produce salt from seawater industrially and to supply it to the soda industry. For this purpose, research and development have been carried out since 1950. The ion-exchange membrane electrodialysis process developed by Tokuyama Soda has been applied to Japanese salt manufacturers and some in Korea and Kuwait.

Tokuyama Soda has developed a total electrodialysis system, which can be applied even to seawater pretreatment, emphasizing not only the improvement of performance but also stable operation in the technological development of the electrodialyzer. We succeeded in developing a revolutionary cation-exchange membrane in which permselectivity to monovalent cation is immobilized on the ion-exchange membranes. The first model of this system was supplied to Sanuki Salt Manufacturing Co., Ltd. in 1986 and has been operating satisfactorily until now, as demonstrated by the following:

– Operations have continued for more than five years with no disassembly or cleaning of the stack as a result of the synergic effect of a new seawater pretreatment technique and the adoption of the CIMS membrane.

– The adoption of the CIMS membrane has made chemical treatment unnecessary. Moreover, the new seawater pretreatment technique has prevented fouling of the membrane surface and therefore has avoided scale trouble. As a result, the operation is very stable.

– The consumption of electricity is very low and the NaCl concentration of produced brine is high. In addition, no aging leading to voltage increases and concentration decreases is experienced.

– Since there is no need for chemical treatment because the CIMS membrane has been adopted, the operation rate is enhanced and the salt content remains high and stable.

INTRODUCTION

Ion-exchange membranes are used in many fields in addition to the salt manufacturing process and are finding a wider application every year. Also, in the field of salt manufacturing for which the development of this kind of membrane was begun in Japan, the performance of ion-exchange membranes such as the supply of low electrical resistance membranes has been improved, the NaCl brine concentration has been raised and the permselectivity to monovalent cations has been improved. At the same time, electrodialyzer techniques have been developed to reduce the thickness of the seawater compartment and the leakage current, and these developments have been incorporated into energy-saving electrodialyzers.

Having hitherto adopted a unit-cell electrodialyzer which was easy to maintain and control, Tokuyama Soda then completed the development of a large-scale filter press electrodialyzer, Type TSW-200, which offers a superior energy-saving performance. Further technical improvements have led to the development of the TSW-200 electrodialyzer system, which consists of an energy-saving electrodialyzer, the TSX-200, (Kobuchi et al., 1987), a seawater pretreatment technique, and the advanced ion--exchange membranes, Neosepta, CIMS and ACS-3. This system has already been supplied to other Japanese salt manufacturers and has been satisfactorily operating since then.

This paper presents the details behind the development of the TSX-200 electrodialyzer system, as well as its outline and operational record, as well as describing its features by using the system supplied to Sanuki Salt Manufacturing Co., Ltd. as an example.

DETAILS OF DEVELOPMENT OF THE TSX-200 ELECTRODIALYZER SYSTEM

Tokuyama Soda supplied a unit-cell electrodialyzer with a production of 180,000 t/year to Kinkai Salt Manufacturing Co., Ltd. and Sanuki Salt Manufac-

TABLE 1

Development of the TSX-200 electrodialyzer system

1976	Start up of pilot plant with a 160 dm^2 filter press type electrodialyzer (TS-160).
1977	Start up of 5,000 t/year electrodialyzer with a TS-160 (160 dm^2) in Kinkai Salt Manufacturing Co., Ltd.
1979	Completion of new ion exchange membranes with a low electrical resistance; trade name: C66-5T, ACS)
	Completion of large-sized new filter-press type electrodialyzer with a 200 dm^2 (TSW-200) Start-up of a new electrodialyzer TSW-200 with a capacity of 17,000 t/year in Kinkai Salt Manufacturing Co., Ltd.
1980	Completion of new ion-exchange membranes with high concentration (C-10 K, A-10 KS)
	Beginning of development for an energy-saving electrodialyzer and seawater filtration system.
1981	Completion of new ion-exchange membranes with a low electrical resistance and high concentration (CIM, A-10 KS)
	Start-up of 5 electrodialyzers (TSW-200, 26,000 t/year) in Sanuki plant (1981–1983)
1982	Contract for supply of process technology, engineering, consultation of construction, electrodialyzer, etc. for the capacity of 50,000 t/year to Petrochemical Industries Company K.S.C. of Kuwait.
1983	Start up of pilot plant with an energy-saving electrodialyzer (TSX-200, 1,220 t/year) in Sanuki plant.
1985	Start up of 28,000 t/year electrodialyzer (TSW-200) in the Sanuki Plant.
	Start up of 28,000 t/year electrodialyzer (TSW-200) in the Kinkai Plant.
1986	Start up of 50,000 t/year electrodialyzer (TSW-200) in Kuwait. (Salt and chlor-alkali plant)
	Completion of new cation membrane with an excellent permselectivity to monovalent ions, and new anion exchange membrane with a low electric resistance (CIMS, ACS-3)
	Completion of TSX-200 ED system
	Start up of 30,000 t/year electrodialyzer (TSX-200) in the Sanuki Plant.
1988	Start up of 30,000 t/year electrodialyzer (TSX-200) in the Sanuki Plant.
1989	Start up of 30,000 t/year electrodialyzer (TSX-200) in the Kinkai Plant.
1990	Start up of 30,000 t/year electrodialyzer (TSX-200) in the Kinkai Plant.
	Start up of 30,000 t/year electrodialyzer (TSX-200) in the Sanuki Plant.

turing Co., Ltd., one of the seven domestic salt manufacturers in Japan during the period 1967–1975. Since then, efforts to develop salt manufacturing technology have been directed towards the reduction of the consumption of electricity and the enlargement of apparatuses. Tokuyama Soda developed a filter-press electrodialyzer to manufacture salt by technically improving the filter-press electrodialyzer which had been used in fields other than salt manufacturing. Moreover, Tokuyama Soda has been successively converting unit-cell electrodialyzers into new filter-press electrodialyzers.

Tokuyama Soda first supplied the TS-160 to Kinkai Salt Manufacturing Co., Ltd. in 1977 and, taking this opportunity, completed an advanced large-scale, filter-press electrodialyzer, the TSW-200, which it later supplied to the above-mentioned two domestic companies as well as Petrochemical Industries Co., Ltd. in Kuwait in the period 1979–1989.

At the same time, we also advanced the development of CIM and A-10 KS ion-exchange membranes and created the low electric resistance for NaCl brine in high concentration.

In response to technical requests to establish energy-saving electrodialyzers to further reduce salt manufacturing costs, Tokuyama Soda continued the development of energy-saving electrodialyzers and seawater pretreatment techniques based on the application of the TSW-200, and succeeded in developing a revolutionary cation-exchange membrane, with a layer of anion-exchange material immobilized on the membrane surface during manufacture to impart permselectivity to monovalent cations. The development of this type of membrane, the improvement in electrodialyzer techniques, and a new seawater filtering technique together led to the completion of a new TSX-200 electrodialyzer system, which was first supplied to Sanuki Salt Manufacturing Co., Ltd. in 1986 and, by 1989, two models to Sanuki Salt Manufacturing Co., Ltd. (Shimamura et al., 1990) and Kinkai Salt Manufacturing Co., Ltd. The details behind the development of the TSX-200 electrodialyzer system are provided in Table 1.

THE TSX-200 ELECTRODIALYZER SYSTEM AND ITS OPERATION RECORD

Flow diagram of the TSX-200 electrodialyzer system

The TSX-200 electrodialyzer system consists of seawater pretreatment facilities which supply clear seawater to an electrodialyzer (ED) and the electrodialysis facilities (Uehara et al., 1986). Figure 1 is a simplified flow diagram of the TSX-200 electrodialyzer system.

The features of the seawater pretreatment facilities are coagulation and two stages of sand filtration which provides high-precision filtering. Raw seawater is added with oxidizing and coagulating agents prior to entering the first sand filter and accordingly, almost all the dead micro-organisms

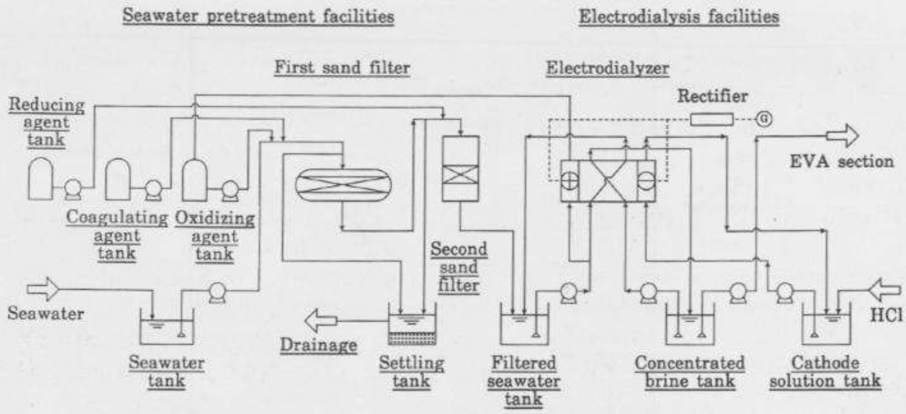

Fig. 1. Flow diagram of the TSX-200 electrodialyzer system.

TABLE 2

Specifications and design performance of the TSX-200 and TSW-200 electrodialyzer

Type of electrodialyzer	TSW-200	TSX-200
1. Specification		
Ion-exchanger membrane (cation/anion)	CIM/A-10 KS	CIMS/ACS-3
Effective area (m^2)	2	2
Thickness between membrane (mm) (dilute side/concentrate side)	0.75/0.50	0.40/0.40
Numbers of membrane (pairs)	3,520	3,520
2. Operation condition		
Current density (A/dm^2)	3	3
Flow rate of seawater (cm/sec)	6	6
Temperature of seawater (°C)	25	25
3. Performance		
Production capacity (t NaCl/Year)	28,200	30,000
NaCl concentration of brine (g/l)	195	205
Power consumed by electrodialyzer (DC-kWh/t NaCl)	195	155

and other turbidity components in the raw seawater are caught and removed by the first sand filter. A secondary filter is provided as a countermeasure against water-quality deterioration in the filtered seawater immediately after the backwash of the first sand filter.

The features of the electrodialyzer facilities are not so different from the convention filter-press electrodialyzer system. However, since this system utilizes the CIMS (Hanada et al., 1990) membrane, it does not require the addition of special chemicals to maintain permselectivity for monovalent cations.

Anode drainage contains Cl_2 and had been accordingly treated with a reducing agent before discharge in the conventional facility; however, the present system effectively utilizes this anode drainage as an oxidizer in the seawater pretreatment facilities.

Seawater pretreatment facilities and the conditions of the treated seawater

The seawater pretreatment facilities in the old filter-press electrodialyzer (TSW-200) use a gravity type sand filter as the first sand filter, and a simplified filtering method, which uses a plastic filtering material as the secondary filter. The performance of the old method in catching turbid material is not good enough to provide satisfactorily precise filtering. Moreover, the old method does not allow fully automatic operation, but rather requires that the filter material be cleaned periodically.

On the other hand, the seawater pretreatment facilities introduction with the TSX-200 results in filtered seawater of superior quality by virtue of its advanced filtering technique and backwash system in addition to its improved filter. Hence, the water quality of the filtered seawater can be evaluated by using the FI (fouling index) value.

Specification and design performance of the electrodialyzer facility

Table 2 compares the specifications and design performance of the TSX-200 and TSW-200 electrodialyzers. The ion-exchange membranes in the TSX-200 electrodialyzer are ACS-3 and CIMS that produce brine with high levels of purity and concentration. The ACS-3 is an improved form of the ACS membrane that has low electrical resistance and produces high salt concentration. The CIMS membrane is an improved form of CIM membrane

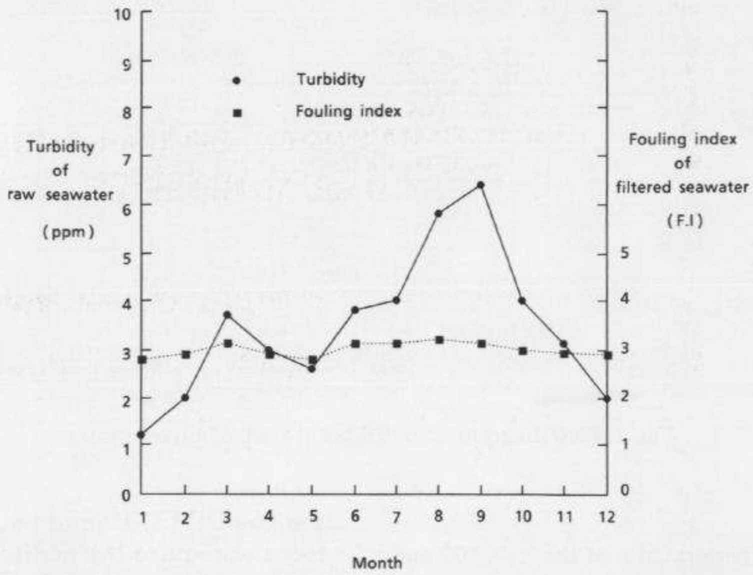

Fig. 2. The annual turbidity level of raw seawater and FI value of the filtered seawater. Represented turbidity unit (ppm) is Kaolin-turbidity unit. FI (fouling index) is equal to SDI (silt density index).

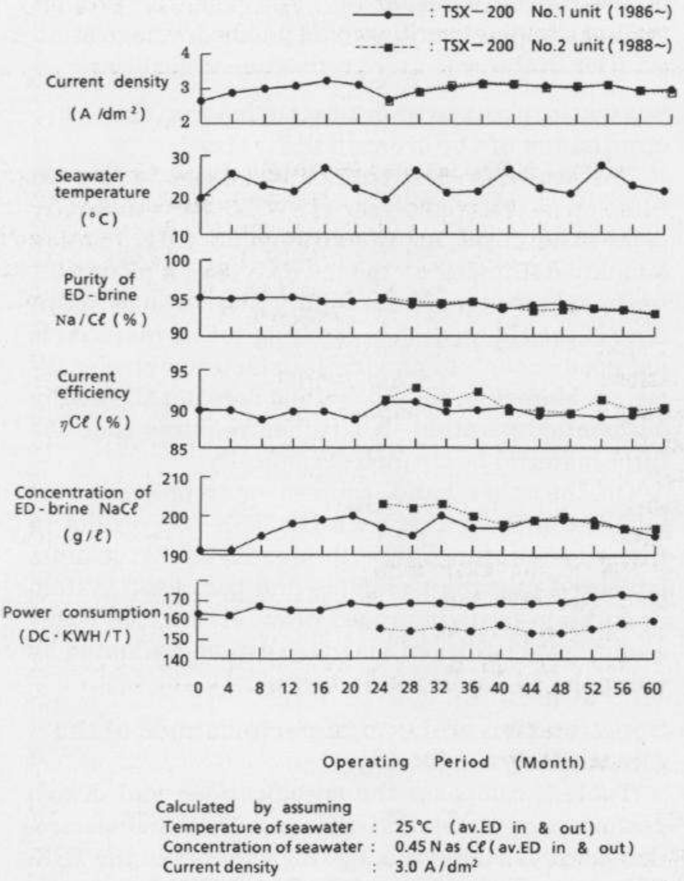

Fig. 3. Operational record of the TSX-200 electrodialyzer.

that had low electrical resistance but required periodic chemical treatment to maintain its permselectivity for monovalent cations. The treatment to impart permselectivity to monovalent cations is thus rendered unnecessary although it had been hitherto performed every several months. As a result, the operation rate and productivity have been enhanced.

Furthermore, a 0.4 mm thick gasket, which makes the thinnest possible dilution and concentration chambers, has been adopted as shown in Table 2.

The reduction of the thickness of the gasket chamber, and the rise in the current efficiency significantly decreases the amount of electricity consumed by dialysis.

Operational record of the TSX-200 electrodialyzer

The No. 1 and 2 units supplied to Sanuki Salt Manufacturing Co., Ltd., were put into service in March 1986 and February 1988, respectively. Their operational records are shown in Figs. 2 and 3. Figure 2 gives the annual turbidity level of raw seawater, as well as the FI value of the filtered seawater. Although the turbidity level of raw seawater changes about 1–7 ppm, the water quality of the filtrate water is always less than 3 FI units, which allows the supply of a stable filtrate throughout the year.

Figure 3 shows the operational record of the electrodialyzer. Particular attention should be paid to the salt content. Due to the adoption of CIMS in which monovalent cation permselectivity has been immobilized, the salt content of the produced brine is high and the deterioration resulting from aging is very slow. The present value of the salt content appears slightly low; however, it can recover its original value if the membrane surface is cleaned be-

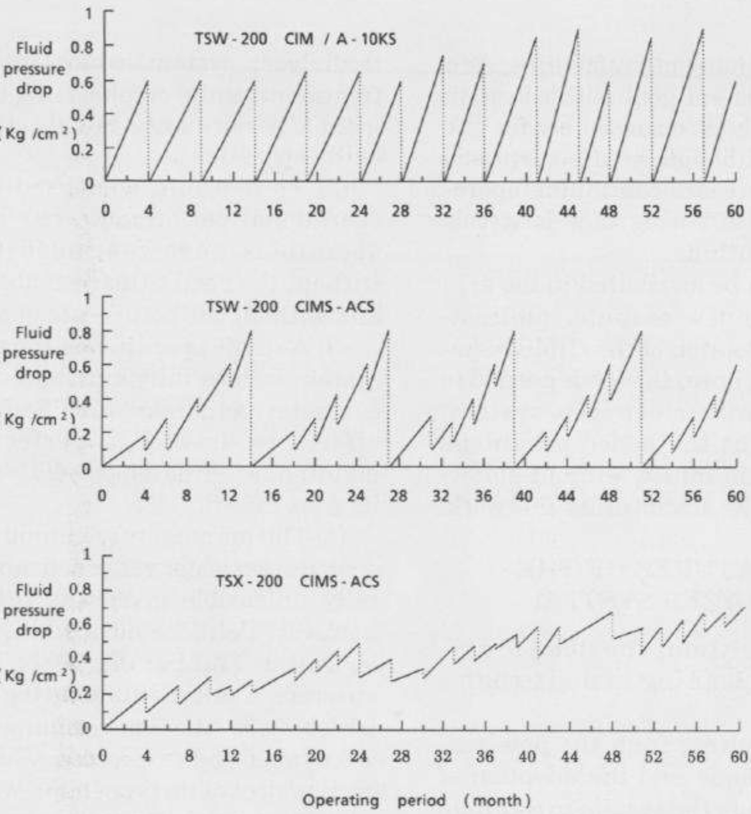

Fig. 4. Fluctuation of fluid pressure drop through the stack in the electrodialyzer.

cause the present state is affected by the fact that the membrane has not been cleaned at all. It is advantageous to avoid disassembly of the membranes, because misalignment or damage of the membranes might cause internal leakage which would effectively reduce the current efficiency.

The current efficiency has been maintained at more than 90% because the leakage current has been decreased by improvements in the unit.

Cleaning the electrodialyzer without disassembly

The filter-press electrodialyzer generally clogs after some time even though the seawater is pretreated, since a minute amount of turbid components remain in the filtered seawater and are gradually deposited on the electrodialyzer membrane surface, distributor plates and spacers. Since the amount of filtered seawater to be supplied to the electrodialyzer is defined in connection with the scale prevention and the utilization factor of seawater, clogging is accompanied by a rise in the fluid pressure drop through the electrodialyzer.

The upper limit of the inlet pressure of the electrodialyzer is determined by its pressure rating and the economical lift of the fluid-feed pump. If the inlet pressure rises to the pump head limit, the fluid flow is reduced, making it necessary to clean the inside of the electrodialyzer. Figure 4 shows the course of the fluid pressure loss in the electrodialyzer. The top graph in this figure indicates the ascending tendency of the pressure in the TSW-200 electrodialyzer. As a result, the stack must be disassembled and cleaned about once every four months.

Next, the graph in the middle shows the tendency of the pressure to rise in the TSW-200 electrodialyzer, in which the CIM cation-exchange membrane is exchanged for a CIMS membrane.

The old CIM membrane required a periodical chemical treatment to maintain monovalent cation permselectivity. This kind of treatment accelerated the contamination of the interior of the stack. The adoption of a CIMS membrane made this permselectivity treatment unnecessary, and mitigated the contaminating speed compared with the upper graph. However, disassembly and cleaning at least once a year is still necessary for the TSW-200 electrodialyzer.

The lower graph illustrates the tendencies of the TSX-200 electrodialyzer. The TSX-200 electrodialyzer has been operating for about five years although only periodical chemical cleaning has been done without any disassembly. Moreover, manual cleaning has not been done even though its seawater chamber is thinner than before. System operation which has not required disassembly for five years is surprisingly successful in general, and it is attracting the attention of many manufactures. As a matter of fact, the development goal of this system was only for operation without disassembly for one to two years. Therefore, although we are surprised by the present situation, we are continuing operations with much interest in seeing how long this wonderful situation can continue.

Our present success can be attributed to the synergic effect created by the new seawater pretreatment technique and the adoption of the CIMS membrane. This success has cut down the labor needed to disassemble and manually clean the system. Moreover, this has brought the added advantage that the membranes remain intact, without suffering the damage which usually accompanies this work.

SUMMARY OF THE FEATURES OF THE TSX-200 ELECTRODIALYZER SYSTEM

Continuous operation without the need for disassembly and stack cleaning in more than five years

The synergic effect resulting from the new seawater pretreatment technique and the adoption of the CIMS membrane permits the system to continue its operation for more than five years from its start without the need for disassembly or stack cleaning.

Stable operation with no scale trouble

Because of the adoption of a CIMS membrane the chemical treatment is unnecessary. Furthermore, the new seawater pretreatment technique almost completely eliminated fouling of the membrane surface, leading to the absence of scale trouble. Consequently, the operation is extremely stable.

Stabilized energy-saving and manpower-saving electrodialyzer operation system

Low consumption of electricity and a high NaCl concentration in the produced brine. No voltage increase and no drop of the NaCl concentration in the produced brine. Operation with limited manpower is made possible because many workers are no longer necessary to disassemble and clean the stack since a fully automated, maintenance-free new seawater pretreatment facility, which does not require such work, has been adopted.

Unnecessary chemical treatment

The adoption of a CIMS membrane has made chemical treatment unnecessary and has raised the operation rate. The salt content of the produced brine is very high and stable.

CONCLUSIONS

(1) Tokuyama Soda has developed a new electrodialyzer system, which includes seawater pretreatment, while emphasizing not only the improvement of performance, but also the improved stability of the operation.

(2) As a result, a marked improvement in the operational performance has become possible and operations have continued for over five years without the need to disassemble and clean the stack and without the occurrence of any trouble.

(3) A stable operation of the unit is essential if the system is to be fully automated by the adoption of a computer, and Tokuyama Soda hopes to extend its efforts to develop a perfectly automated and maintenance-free electrodialyzer system based on its past record.

(4) The manufacture of industrial salt by the present system is not yet practicable since it is economically unfeasible given the price of imported salt; however, Petrochemical Industries Company (PIC) in Kuwait (Tani et al., 1985: Tomita, 1988) is constructing a salt manufacturing and electrolysis firm which uses the ion-exchange method based on Tokuyama Soda's process. This project is the first such project of its type in the world and is attracting a lot of attention. Smooth operations have continued from the start in 1986 to the present, except for the unhappy period of the Iraq invasion. (We believe operations were suspended for four to five months.) Tokuyama Soda is proceeding with its development of the electrodialyzer system for use in the production of industrial salt using the ion-exchange membrane method, and is being encouraged by the valuable experience of this PIC.

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