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The High Performance Electrodialysis Process for Concentration of Seawater

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ABSTRACT

The electrodialysis technique is used in the field of seawater concentration, brackish water desalination, purification of pharmaceuticals and foodstuffs, re-use of waste water and various electrolysis processes.

Asahi Glass Co. has achieved improved operation and concentration and a reduction in construction costs. We have actual experience with this process through construction and operation of two large commercial salt manufacturing plants. Our electrodialysis process has several special features compared with the existing conventional process. This excellent performance has been achieved by developing the structure of the electrodialyzer, gasket, and new membranes.

INTRODUCTION

Ion-exchange membranes, which are the basis of the electrodialysis technique, have been developed for 40 years. During this time the development of brackish water desalination in Europe and America and seawater concentration in Japan has been carried out. Seawater concentration needs higher membrane performances than does the desalination technique, e.g. low electric resistance, high current efficiency, high concentration of seawater and high univalent ion selectivity. By meeting these needs, the Japanese electrodialysis technique is now the best in the world and is used in the field of seawater concentration, brackish water desalination, purification of pharmaceuticals and foodstuffs, re-use of waste water and various electrolysis processes.

All table salt in Japan is now being produced by the electrodialysis seawater concentration technique and the final target is to supply raw salt to the chlor-alkali factories. Already a step has been taken towards this goal and the process has been improved through research and development activities.

Asahi Glass has been developing the electrodialysis process for 40 years. At the end of 1970s, we developed an improved electrodialysis process, mainly for the reduction of energy consumption and the improvement of operation and construction costs. The process was commercialized in 1980, replacing existing conventional plants and we have over 10 years' actual experience with this process through construction and operation of two large commercial salt manufacturing plants. Furthermore, we have now succeeded in developing more energy-saving technology. Our electrodialysis process has as its main features low energy consumption, with high concentration, high brine purity and simple, stable operation compared with the existing conventional process.

The special features of the electrodialysis process may be compared with the solar field process for Japanese domestic conditions. The solar salt field technique is similar to the agricultural method whereas the electrodialysis process is industrial. The special features of the electrodialysis process are shown in Table 1.

PRINCIPLE OF ELECTRODIALYSIS

An ion-exchange membrane has the ion permselectivity to allow selective permeation of cations in the cation-exchange membrane and anions in the anion-exchange membrane. Electrodialysis can dilute or concentrate the electrolyte solution by using

TABLE 1

Features of the electrodialysis process

Items	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

DC electricity. As this process is performed continuously, regeneration is not needed during operation. Figure 1 shows the principle of the technique. In an actual multi-cell type electrodialysis unit, multiple cation and anion-exchange membranes are installed alternately and a pair of electrodes are arranged at both ends of cells. Concentration and demineralization proceed simultaneously in the unit. The typical application for concentration is seawater concentration and the typical application for demineralization is brackish water desalination.

The table-salt manufacturing process by electrodialysis is basically composed of the electrodialysis seawater concentration process and the evaporating crystallization process. Firstly, 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 Fig. 2.

Energy costs represent a high percentage of the cost of table-salt manufacture. The reduction of electricity consumption in the electrodialysis process and steam consumption in the crystallization process, i.e. increase in the concentration of concentrated brine in the electrodialysis process, are significant.

DEVELOPMENT OF THE SEAWATER CONCENTRATION TECHNIQUE

The basic concepts of the development of the seawater concentration technique using electrodialysis are shown in Fig. 3. The first is low energy consumption. Special design improvements of the membrane and the electrodialyzer decrease electricity con-

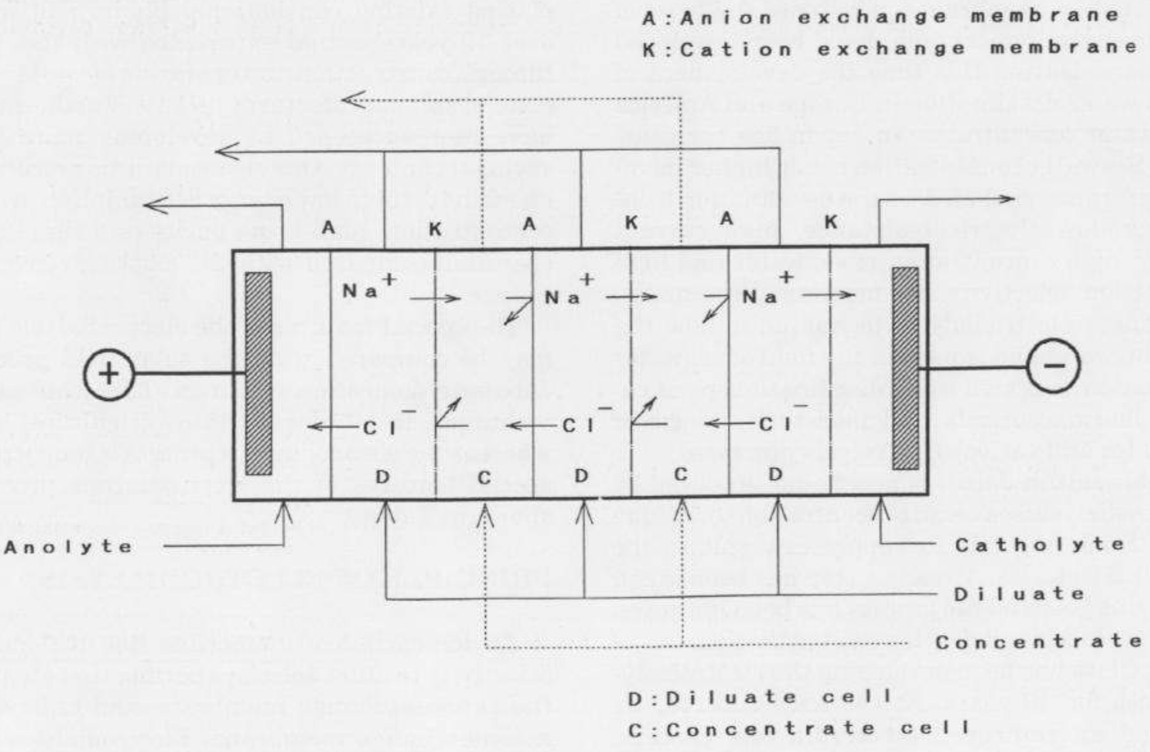

Fig. 1. Principle of electrodialysis (example: NaCl solution).

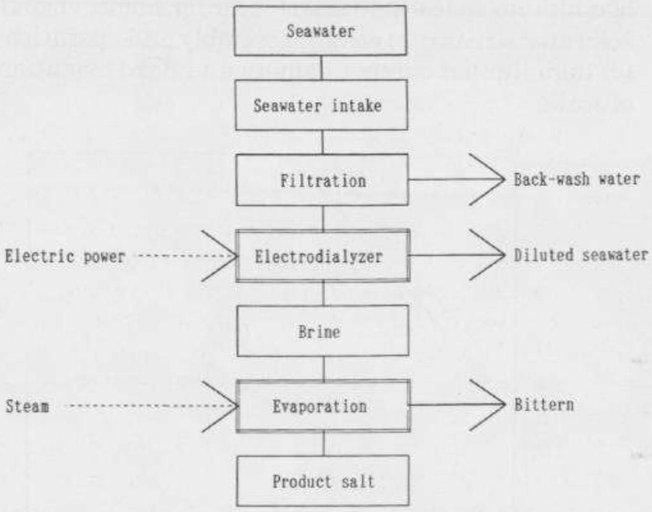

Fig. 2. Salt manufacturing process.

sumption in the electrodialysis process. Furthermore, the high sodium chloride content in the brine reduces steam consumption in the crystallization process. The second is long-term stable operation enabled by the improvement of the pretreatment process. In addition, the improvement of the inner structure of the electrodialyzer enables the electrodialysis unit to be operated continuously and easily. The third is that the special design and material of the electrodialyzer allows easy maintenance. The points of development are given below.

Development of low electric resistance membrane

The basic characteristics which influence the performance of ion-exchange membrane, for example, electric resistance and current efficiency are water content W (g H_2O/g wet resin), ion-exchange capacity A_R (meq/g dry resin) and fixed ion concentration A_W (meq/g H_2O). A_R is determined as the density of ion-exchange unit on the stage of macromolecule synthesis. W is the amount of water in the membrane soaked in water. A_W is determined by A_R and W and is the concentration of fixed ion in the case where the membranes is assumed to be a polyelectrolyte. The relationship between A_R, W and A_W of a styrene-divinylbenzene type membrane has been shown in Fig. 4 by Itoi (1981) and Yawataya (1982).

In general, the water content is proportional to the ion-exchange capacity. The higher water content causes more swelling of the membrane. However, at the same ion-exchange capacity, the increase in amount of crosslink agent — divinylbenzene — causes the advance of a three-dimensional network construction and decreases swelling. The result is fixed ion concentration increase and permselectivity of the membrane progress. At the same time, electric resistance increases. Therefore, optimum composition should be selected in order to fit the requirements. In Fig. 4, region I shows the condensation membrane of phenol-formaldehyde type. The membranes of region I →II → III have been developed successively. Nowadays, a styrene-divinylbenzene

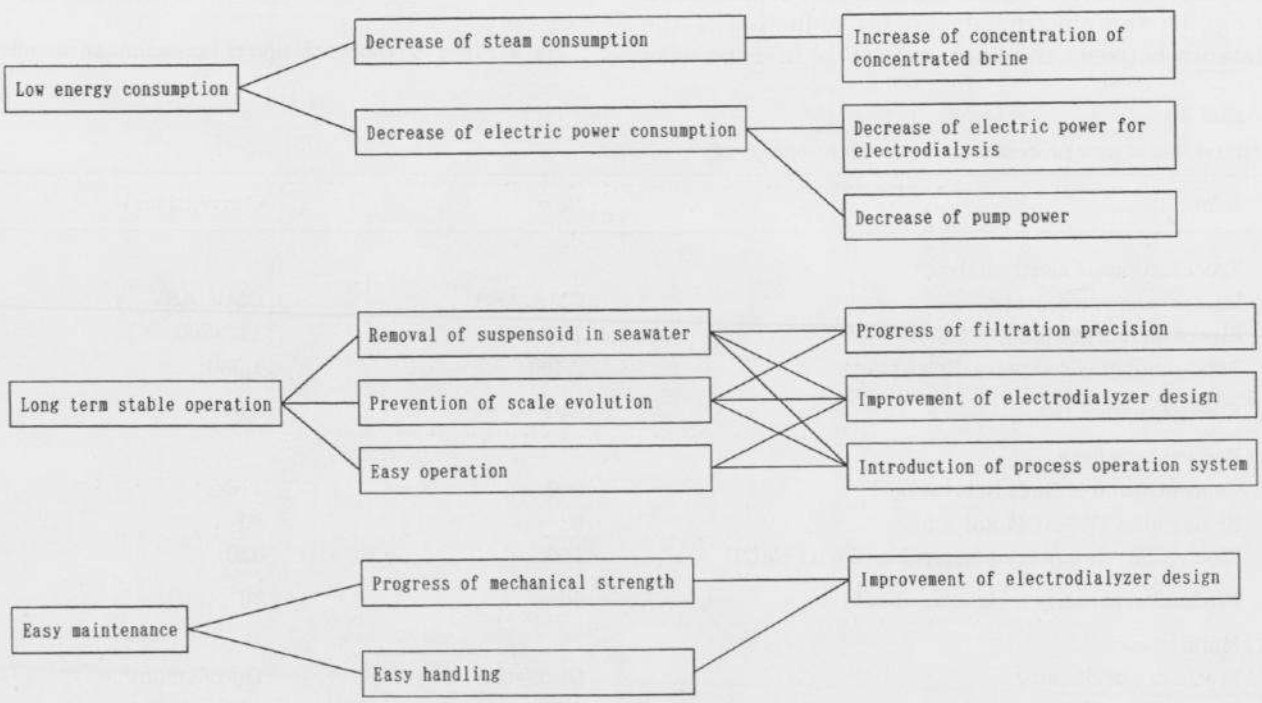

Fig. 3. The basic concept of the development of the seawater concentration technique.

type membrane is typical.

Improvements to the ion-exchange membrane consist of fabric, composition of resin and surface treatment.

The fabric was developed with the fabric manufacturer. The fabric and composition of the ion-exchange resin were investigated with the fabric sample. The composition influences electric resistance of the membrane and the concentration of the concentrated brine. Many kinds of ion-exchange membrane were made and the special membranes were then established.

Surface treatment of the ion-exchange membrane is performed to reduce the permeation through the membrane of Ca^{2+}, Mg^{2+} and SO_4^{2-}, which are unnecessary components in seawater for table salt. If gypsum permeates into the concentrate chamber, it is deposited not only in the concentrated brine but also on the membrane itself. However, the surface treatment employed increases the electric resistance of the membrane. Research is needed to ascertain the optimum conditions. Univalence permselective membranes have been developed by treating the cation-exchange membrane with cationic polyelectrolyte solution (Tanaka and Seno, 1981; Sata and Izuo, 1990).

Optimum electrodialyzer construction

The following features are required of the electrodialyzer for salt manufacture: (1) low energy consumption; (2) high concentration of produced brine; (3) large production capacity per unit of the electrodialyzer. The following conditions must be met when designing the electrodialyzer: (a) reduction of the distance between the membranes; (b) investigation of optimum spacer and distributor for homogeneous seawater stream; (c) ease of assembly and operation; (d) high limited current density and hard evolution of scale.

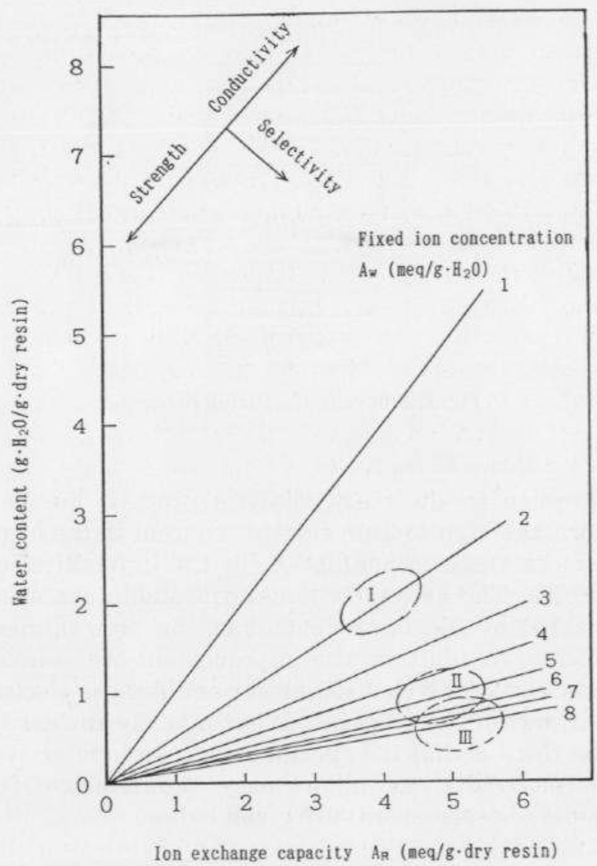

Fig. 4. Fixed ion concentration of ion-exchange membrane.

TABLE 2

Comparison of new process with the conventional type

Items	New	Conventional
1. Specifications of electrodialyzer		
Ion exchange membrane	CMS, ASS	CMV, ASV
Size of membrane (cm)	112×230	112×200
Total number of cell pairs (Pairs/block)	2,400	1,350
2. Electric current (A)	540	540
3. Performance data		
Concentration of NaCl in brine (g/l)	200	170
Brine purity (% NaCl/total salt)	93	89
Electrodialysis power consumption (KWh/t·NaC1)	150	320
4. Production capacity (t·NaCl/day·block)	56	33
5. Maintenance		
Frequency of cleaning	Once/year	Once/3 months
Membrane replacement	1%/year	10%/year

In order to satisfy these conditions, the following points are investigated:

(a) Selection of materials: High electric insulation, low coefficient of thermal expansion, high chemical resistance, proper elasticity and easy workability.

(b) Molding technique: The thickness of the gasket is less than 1 mm. Maintaining the mechanical strength tends to make the mold complex. Precision is required to make the complex mold.

(c) Low number of parts: In order to simplify the handling, it is necessary to reduce the number of the parts. Therefore, a technique combining the different materials is needed.

(d) Manufacture of the chamber and intermediate: One block of electrodialyzer is subdivided into several stacks at the point of handling. An injection molding technique of FRP for the chamber and intermediate is required.

(e) Prevention of inner and outer leakage: Rib is molded on the surface of the gasket in order to prevent leakage of the inner and outer solution. A molding precision is needed.

(f) Light weight: The chamber and intermediate are made of FRP. In order to lighten the electrodialyzer, a light material must be used.

SPECIAL FEATURE OF THE ASAHI GLASS ELECTRODIALYSIS PROCESS

The Asahi Glass electrodialysis process has several special features compared with other conventional processes. Its excellent performance, as described below, was achieved by developing the structure of the electric cell, gasket and new membranes.

(1) Largest production capacity

The largest ion-exchange membrane size of over 2 m^2/sheet and the large number of approximately 2,400 pairs or more of membranes installed in a unit enables annual production of around 20,000 t or more of salt in one block of the electrodialyzer.

(2) Low energy consumption

The special design improvements of the membrane and the electrodialyzer reduce electricity consumption in the electrodialysis process. Moreover, the high sodium chloride content in the brine reduces steam consumption in the crystallization process.

(3) Simplicity of the plant and high utilization of seawater

The inner design of the electrodialyzer enables high recovery of salt from seawater by a single-stage and single-pass system of seawater in the dilute chamber. Thus, there is no need to recycle seawater in the unit and plant design is substantially simplified.

(4) Ease of operation

Because the plant design is simple, the electrodialyzer can be operated by only a few persons using simple automatically-controlled systems.

(5) 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. The frequency of 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 conventional methods.

A comparison of the new process with the conventional type is given in Table 2.

The following benefits could be realized as a result of the development.

(1) Production capacity is increased by about 70%.

(2) Electric power consumption is reduced by about 53%.

(3) Concentration of NaCl in brine is increased by about 13%.

(4) Brine purity is increased from 89% (NaCl/total salt) to 93%.

(5) Operation and maintenance are simple. Long and stable operation over a year is expected and membrane replacement is reduced.

OPERATION RESULTS

Figure 5 shows a photograph of the new electrodialyzer and its exterior view is shown in Fig. 6. Figure 7 illustrates the isoenergetic curve, prepared by Japan Tobacco Inc. It is assumed that 2.6 t of water can be evaporated with 1 t of steam, with the use of triple-effect evaporators and that the electric power unit price is ¥17.6/kWh, heavy fuel unit price ¥58.4/l, heavy fuel consumption 70 l/t ton of generated steam.

In Fig. 7, the energy cost of the conventional 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 '–'. It is difficult to understand that the energy cost of the new process is ¥4,300/t less than that of the conventional process. As heavy fuel oil prices rise, the new process becomes even more cost-effective than the conventional process.

CONCLUSIONS

The performance of the electrodialysis process for concentration of seawater is discussed. High performance was achieved by developing the structure of the electrodialyzer, gasket and new membrane.

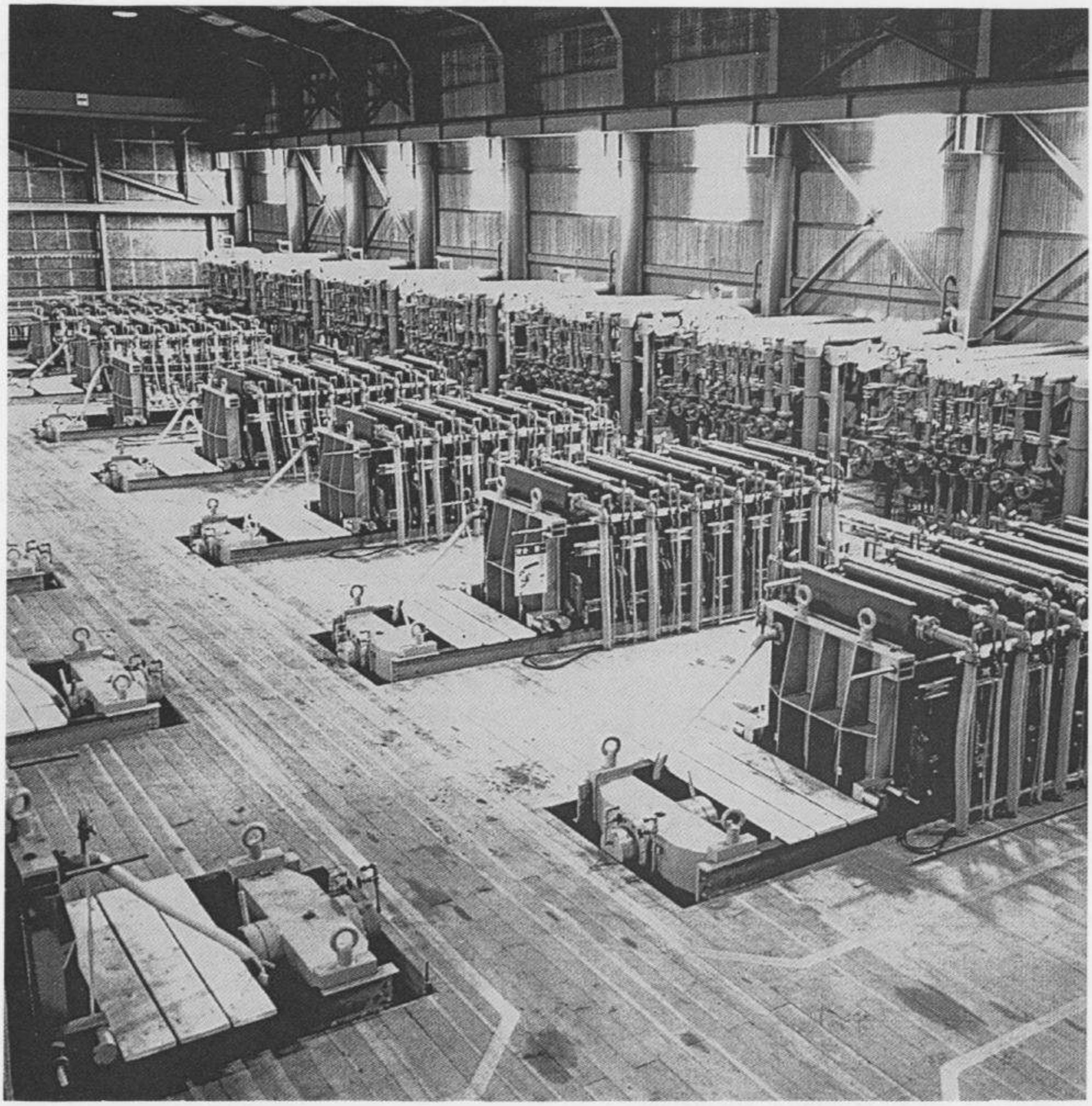

Fig. 5. Photograph of new electrodialyzer model CS-V.

The ion-exchange membrane has a long history among the various functional membranes. Hereafter, new materials and new concepts will be introduced to ion-exchange membranes and the electrodialysis technique will progress further.

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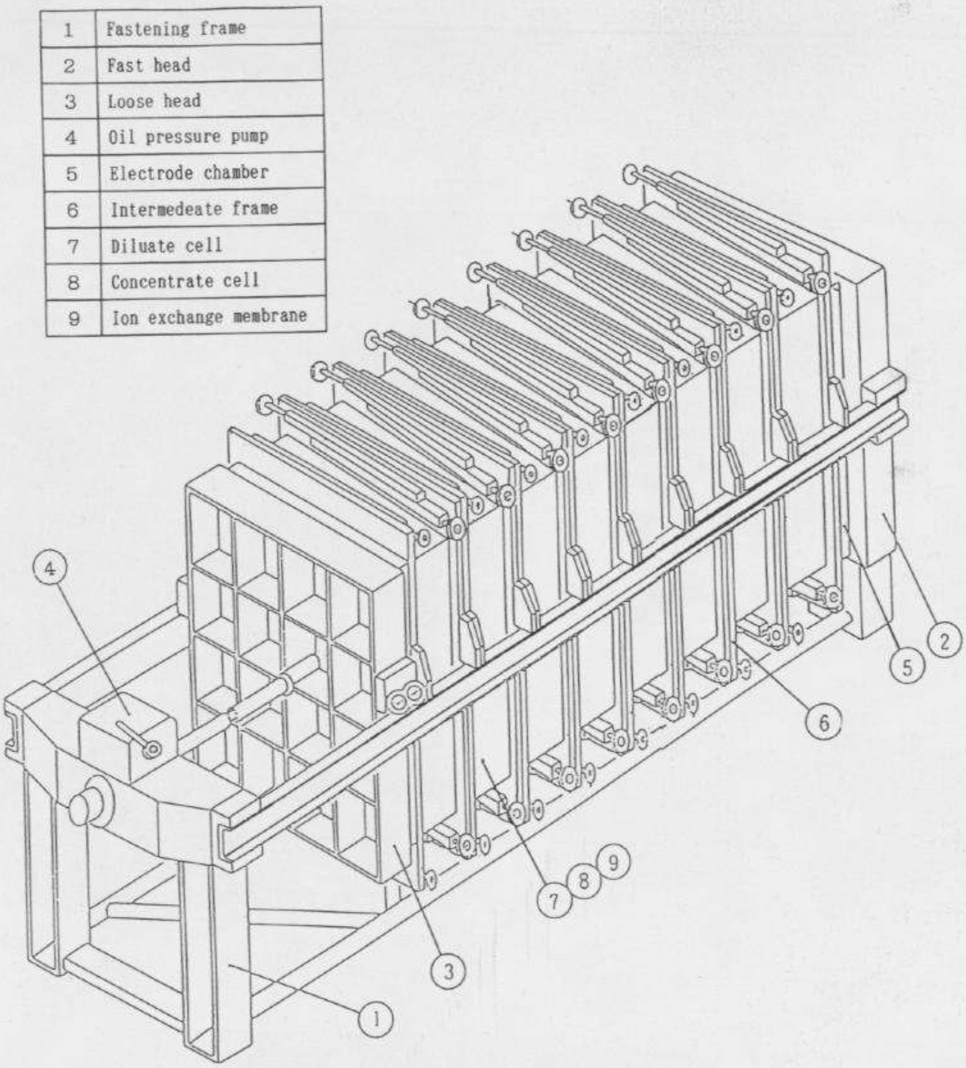

Fig. 6. Model CS-V electrodialyzer.

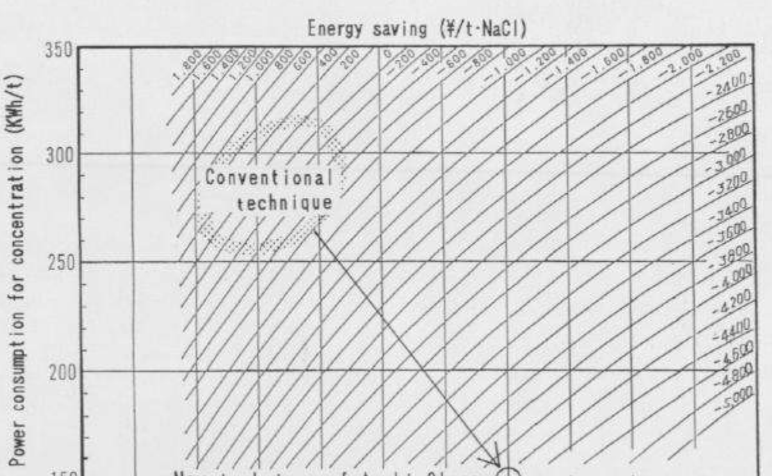

Fig. 7. Comparison of energy cost in electrodialysis process. Concentration of concentrated brine (NaCl g/l). Electricity, ¥17.6/kWh; fuel, ¥58.4/l; evaporation, 2.6 t water/t steam.