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Recent developments of the chlorine industry in Japan

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In response to the June 1986 time limit the conversion of mercury (M-process) cells to ion exchange membrane (IM-process) cells is now well advanced in the Japanese chlor-alkali industry. In parallel with this, many asbestos diaphragm cell (D-process) plants have also been converted to the membrane process (DI-process). These successive conversions are indicative of an acknowledgement of the economies inherent in the IM-process as a result of technical improvements. This article gives an account of the recent developments and progress of the IM-process in Japan.

1. Conversion sequence of processes for chlor-alkali manufacture in Japan

The Japanese chlor-alkali industry was forced to convert all M-process plants into the D-process as a result of a political decision arising from the occurrence of Minamata disease and the consequent 'mercury dispute' of June 1973. In addition, the 'oil crisis' of October 1973 completely upset the Japanese economy causing a sharp decrease in domestic demand. The heavy burden of capital investment as well as soaring energy costs caused the Japanese chlor-alkali industry to lose its international competitive edge.

Under the circumstances, efforts were directed to the development of the 'closed system' [1] version of the M-process plant and to the improvement of the D-process which brought fitting rewards. In spite of the implementation of the closed system, however, the continued operation of the M-process plant was not permitted, although the D-process was still unsatisfactory in view of its high energy consumption and poor product quality. The development of a superior process became a matter of urgency.

Such market requirements were met by the successful development of the IM-process plant followed by improvements stimulated by the IM-process Evaluation Committee which, in 1979, judged that industrial application would be feasible. At the 9th meeting of the Committee for the Protection of the Environment from mercury, etc. held in December 1983, the final decision was made that the conversion must be completed by the end of 1984 except for those plants with unavoidable difficulties for which the time limit was prolonged until the middle of 1986 at the latest.

As stated above, the conversion was initiated as part of Government policy for the protection of the environment. Recently, however, it has been continued for economic reasons with no relation to the pollution problem. The sequence of the process conversion starts from the M-process leading to the D-process and further from the D-process to the DI-process or the IM-process. In some cases M-process plants were converted directly to the IM-process. By the end of June 1986, the M-process plants will have been completely phased out from the Japanese chlor-alkali industry.

Table 1 [2] shows the change in the production capacity following the conversion.

2. IM-process

2.1. *Development of high performance membranes*

The performance of the ion exchange membrane is, of course, crucial to the success of the IM-process. Since the first manufacture of an

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Table 1. Changes in production capacity (tons per month) by process over the period May 1984 to June 1986

	Hg process	*Asbestos diaphragm process*	*Membrane process*	*Total*	*Remarks*
Actual production capacity – end of May 1984					
Original Hg process plants (22 plants in 18 companies)	108 121	45 325	43 210	196 656	One plant in one company less compared with June 1983.
Non-Hg process plant (29 plants in 23 companies)	0	133 501	45 301	178 802	One plant in one company added compared with June 1984.
Total (51 plants in 34 companies)	108 121 (28.8%)	178 826 (47.6%)	88 511 (23.6%)	375 458 (100%)	
		(71.2%)			
Expected production capacity – end of December 1985					
Original Hg process plants (13 plants in 10 companies)	56 394	27 136	6 125	89 655	Nine plants in eight companies less compared with May 1984. Among them, one plant in one company not converted and shut down.
Non-Hg process plant (37 plants in 29 companies)	0	129 290	140 547	269 837	Eight plants in six companies added compared with May 1984
Total (51 plants in 34 companies)	56 394 (15.7%)	156 426 (43.5%)	146 672 (40.8%)	359 492 (100%)	
		(84.3%)			
Expected production capacity – end of June 1986					
Non-Hg process plant (48 plants in 34 companies)	0	145 353 (41.8%)	202 668* (58.2%)	348 021 (100%) (3 533 000 tons per year)†	Compared with December 1985. Three plants are shut down and absorbed into other plants.

* DI-process and HI-process account for 32.5% (65 862 tons per month), corresponding to 18.9% of the total capacity.

† Calculation basis of annual production capacity: monthly capacity × 12 × 0.846.

ion exchange membrane by Willie and Juda in 1950, successive improvements have led to higher performance. In its early form the standard membrane was of the hydrocarbon type [3]. Although many researchers tried to adapt this membrane for brine electrolysis for chlor-alkali production they failed because the C–H bond of the membrane was instantly oxidized and it lasted only a few hours in use. Around 1968, Du Pont's perfluorocarbon membrane, Nafion (R), broke the deadlock, followed by successive improvements for chlor-alkali application. Recently, membrane performance has been dramatically enhanced.

2.1.1. Production of high exchange capacity membrane. Generally speaking, the greater the ion exchange capacity of the membrane, the higher the electric conductivity and the stronger the caustic soda solution which can be produced at high current efficiency. However, it proved quite difficult to manufacture perfluorocarbon membrane (F-membrane) with a large ion exchange capacity. The F-membrane is typically composed of tetrafluoroethylene (TFE) and hexafluoropropylene oxide (HFPO), having a linear polymer structure as shown in Fig. 1. Since it has no bridge structure, swelling and shrinkage is suppressed by the crystallization of $-(CF_2-CF_2)_X-$ [4]. However, if the exchange capacity is increased, the X portion is correspondingly decreased resulting in reduced mechanical strength of the membrane. For instance, with Nafion, if $m \geqq 1$, $n = 2$, $X = SO_3^-$ and with equivalent weight (EW) below 100, the membrane becomes swollen with water and the manufacture of such a membrane is impractical.

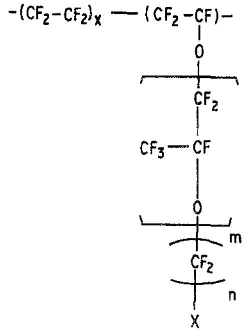

Fig. 1. General formula of perfluorinated polymer ion exchange membrane. X = ion exchange groups such as SO_3H, COOH, etc.

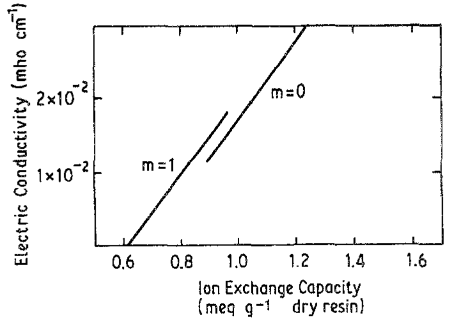

Fig. 2. Ion exchange capacity of perfluorosulphonic acid membrane versus electric conductivity in 25° C, 0.1 N NaOH.

Therefore in order to increase the exchange capacity while keeping the X portion within a proper range, the molecule must have short side chains. Recently, membranes with large exchange capacity have been synthesized by controlling 'm' and 'n' for required membrane properties, such as flexibility, while maintaining X within a certain range (Fig. 2) [5].

In addition, by increasing the molecular weight to the order of hundreds of thousands and changing the ion exchange group from sulphonic acid to carboxylic acid, a polymer with an exchange capacity as high as 1.9 meq g^{-1} can be manufactured without swelling. Membranes manufactured in such a way have ion exchange capacities larger than the sulphonic acid type membrane and higher electric conductivities. (Fig. 3) [5].

2.1.2. Multi-layer membrane. The sulphonic acid-type membrane has high electric conductivity and low potential drop, but also has disadvantages. The sulphonic acid-type membrane

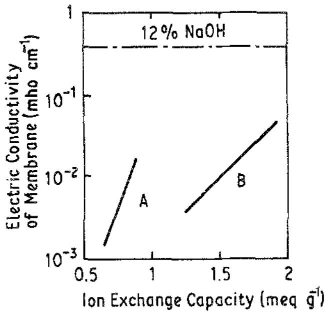

Fig. 3. Ion exchange capacity versus electric conductivity. (A) Sulphonic acid membrane. (B) Flemion (carboxylic acid membrane).

(which is strongly acid) has a large moisture content and the concentration of exchange groups in the membrane cannot be increased. Therefore once the concentration of caustic soda solution in the cathode chamber rises, current efficiency drops sharply. To eliminate these disadvantages, a membrane with a small exchange capacity was bonded to form a two-layer laminate. The performance was, however, not as good as expected, i.e. 17% caustic soda concentration and 80% current density [6].

It has been known from an early stage that the carboxylic acid-type membrane is chemically stable and that its current efficiency is high [7]. However, due to low electric conductivity and weak acidity the carboxylic acid-type membrane, in the presence of acid, tends to become non-dissociable, losing its ion exchange function. As a result it is difficult to control the O_2 content in Cl_2 or the generation of chlorate ions with this type of membrane.

With the above knowledge, a two-layer membrane having a sulphonic acid layer on the anode side and carboxylic acid layer on the cathode side was developed. The required thickness of the carboxylic acid layer is as little as 10–20 μm [4, 8] (Fig. 4); the surface of the sulphonic acid layer is modified by chemical treatment to form the carboxylic acid layer, rather than adding a separate membrane by lamination [9]. As an alternative, a laminated two-layer membrane comprising carboxylic acid membranes having different exchange capacities was also developed [5]. However, in this case, pH control during the addition of hydrochloric acid to the anolyte is important since it is a carboxylic acid membrane.

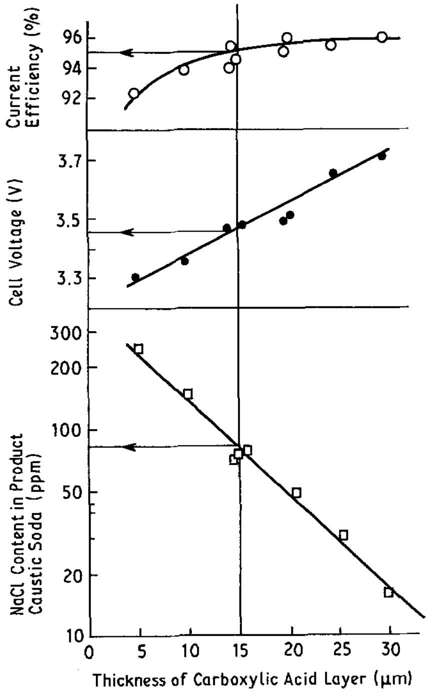

Fig. 4. Effect of carboxylic acid layer thickness. (Neosepta FC-1000; 2kA m^{-2}; 6 N NaOH; 80° C.)

As a result of the development of composite forms, membranes having high exchange capacity, low voltage drop and current efficiency as high as 95–96% have become available.

2.1.3. Reduction in membrane thickness and improved physical strength. The electric conductivity of the membrane is one-twentieth of that of the solution. A thinner membrane is preferable to optimize electric conductivity; however, thin membranes are of low physical strength and also tend to permit salt transfer causing poor quality of the caustic soda produced (Fig. 5) [10]. To maintain the necessary physical strength, reinforcement with polytetrafluoroethylene (PTFE) cloth backing or the addition of micropore cloth is adopted. A composite membrane of about 250 μm thickness is typically used in practice.

2.1.4. Zero gap design. One of the key factors influencing cell voltage is the electrical resistance of the fluid (which may include bubbles) in the interelectrode gap. To decrease this the membrane is brought close to the electrode; however, if the interelectrode gap is less than 1 mm, the cell voltage begins to rise (Fig. 6) [10]. Such increase is caused by adhesion of evolved gas to the membrane surface which interferes with the

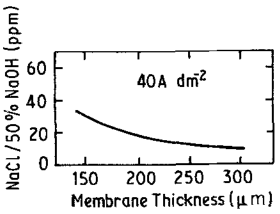

Fig. 5. Membrane thickness versus NaCl content.

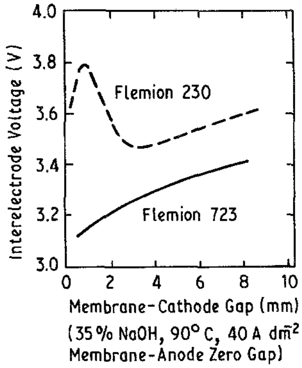

Fig. 6. Membrane cathode gap versus interelectrode voltage. (35% NaOH; 90° C; 40 A dm^{-2}; membrane–anode zero gap.)

release of gas bubbles, especially H_2, from the membrane surface.

Closer proximity of the electrodes causes a number of adverse effects such as shortage of Cl^- at the electrode surface, O_2 generation by OH^- discharge and attack of alkali on the anode coating. The most important requirement is to promote the release of H_2 bubbles. Among the means of achieving this are (a) the preparation of a rough membrane surface during manufacture, (b) making the membrane more hydrophilic by the formation of a thin porous layer of non-conductive inorganic material on its surface [11], (c) to modify the cathode chamber or electrode configuration and (d) to develop techniques to optimize the electrolyte velocity. In addition to these, increase in the effective membrane area, decrease of current density, and uniform current distribution are combined to enable the interelectrode gap to be reduced to zero.

2.2. *High performance anode*

The anode used for the IM-process needs to be alkali resistant since it is in contact with an alkaline membrane in 'zero gap' operation. To enhance its alkali resistance the anode coating is modified by the addition of special metals in addition to ruthenium in the state of solid solution (Fig. 7) [12]. The anode life, which is normally recognized to be 7 years, can be prolonged to about 9 years. Furthermore, to lower the O_2 content in Cl_2, dimensionally stable anodes (DSA) with high oxygen overvoltage or PdO_2-type electrode coatings are under development.

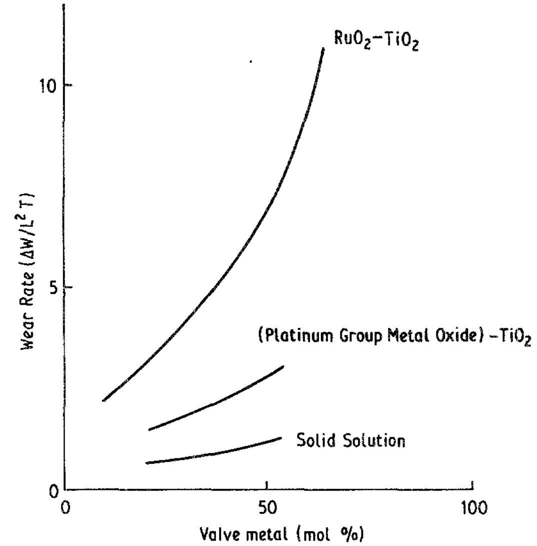

Fig. 7. Corrosion resistance of solid solution electrode.

The variation of current distribution with the shape of the anode has been investigated using the ^{45}Ca isotope, and an optimum hole diameter has been determined (Fig. 8) [12]. Using that diameter, the effective membrane area over which current actually flows increases and reductions of current density and voltage are achieved.

On the other hand, flexible mesh-type electrodes have also been developed. The membrane is attached over the whole area of the electrolysis surface of the electrode in an attempt to achieve uniform current distribution.

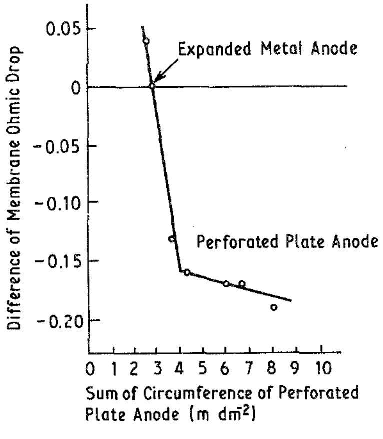

Fig. 8. Sum of circumference of perforated plate anode versus difference of membrane ohmic drop. Membrane: Asahi Chemical (EW = 1350). Current density: 5 kA dm^{-2}. Operating temperature: 90° C.

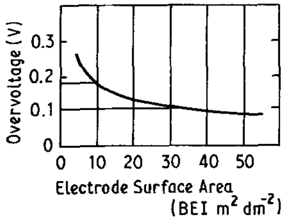

Fig. 9. Electrode surface area versus overvoltage by nitrogen absorption method.

2.3. *Activated cathode*

The need for energy saving has promoted the development of an activated cathode with a hydrogen overvoltage lower than that of the present steel cathode.

The methods applied for activation include the formation of an electroplated nickel–Raney nickel composite layer on the steel surface [5] or the utilization of a catalyst consisting of the oxide of a transition element. By these methods the electrode surface area is increased to 30–40 $m^2 dm^{-2}$ (Fig. 9) [5].

To maintain activation, a catalyst stabilizer is added to prevent metal oxides from being reduced to the metal and to prevent iron from forming and depositing in the electrolyte. The current supply must also be rigidly controlled.

Over several years of operation it has been shown that these methods achieve a reduction of hydrogen overvoltage of between 0.1 and 0.2 V (Fig. 10) [12]. Recently, improvements have also been made to prevent loss of activation by current reversal which occurs at the time of short circuiting or power failure.

2.4. *Electrolysers*

There are two types of electrolyser for the IM-process, i.e. the monopolar type and the bipolar type, each having unique design features.

The monopolar type is relatively easy to construct. The number of cell units in each electrolyser (which determines the current loading) and the number of such electrolysers in circuit can be chosen to suit the characteristics of the available rectifier and the production required.

For the cell construction there are two design concepts: a design in which the supply and drain lines to and from each cell unit are incorporated in the cell to simplify connections to the electrolyser, and an alternative design in which the supply and drain to and from each cell unit are through manifolds to enable a watch to be kept on the flow in and out of each cell and to check for faulty membranes. In both designs, the liquid inside the electrolyser is in natural (as distinct from forced) circulation.

Considering that the monopolar cell typically has wide current bus bars, the cell employs a design of cell units with small membranes in which the capacity per electrolyser is expanded by increasing the number of cell units while, in the alternative design, large cell units are used and the voltage drop is minimized by a conductor rod and distributor with which each cell unit is equipped.

In the bipolar type, manufacture of a large size electrolyser is relatively easy. In fact, an electrolyser with a capacity as large as 20 000 tons per year has been built. In addition, the current distribution can easily be made uniform with little bus bar voltage loss. However, the cell construction is complicated. Each individual cell unit must be fed and drained of product. Forced circulation of the electrolyte to prevent electrolytic corrosion requires an external power system.

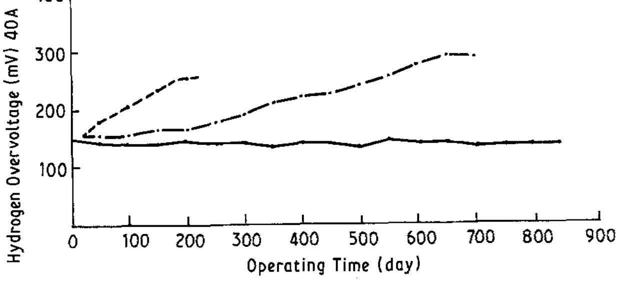

Fig. 10. Change of H_2 overvoltage with time. – – –, porous nickel; – · –, porous nickel oxide; ——, Asahi Chemical activated cathode.

As mentioned above, monopolar and bipolar types each have advantages and disadvantages and selection is not always easy. Comparative evaluations are necessary in respect to plant capacity, new plant installation or conversion from the existing plant, utilities cost, unit consumption, membrane, anode and cathode cost, operation and maintenance of the electrolyser, product quality, etc.

2.5. *Secondary brine purification*

Stable operation of the IM-process is largely governed by the quality of feed brine. Calcium and magnesium in the feed brine will accumulate within the membrane causing damage or reduction in exchange capacity. The tolerable range, which varies with NaOH concentration, may be below 20 p.p.b. when making 35% NaOH [13].

To secure high quality brine a combination of two-stage or three-stage chelate resin towers with the conventional brine purification system is employed. A chelate resin with a large capacity for selective Ca–Mg adsorption has been developed to reduce the content to below 20 p.p.b. In addition, in order to optimize the function of the resin, pH, temperature, SV, LV, conditions for regeneration, and other factors have to be taken into account and a fully automated operation system has been developed. Needless to say, for the stable operation of the secondary brine purification system it is essential that the brine from the primary purification system is also of uniform quality.

For the detection of Ca–Mg below 20 p.p.b., atomic adsorption spectroscopy using a graphite furnace-type analyser operating on the principle of the Zeeman effect or the ICP method is employed. For on-site plant monitoring, a field unit capable of analysing in the order of 100 p.p.b. at one tower outlet has been developed. With present systems, 30 p.p.b. seems to be the detectable limit. Analysers for levels below 20 p.p.b. are presently in the research stage at several companies.

2.6. *Evaporation system*

The concentration of caustic soda produced by the IM-process is in the range of 20–35% NaOH, which must usually be evaporated to 50% NaOH for commercial application. A D-process evaporator is poorly suited to this duty since it is designed to concentrate a weak caustic solution containing about 12% NaOH and a similar quantity of salt. Because of the inevitable deposition of salt, the evaporator is usually of a forced circulation type, which requires an elaborate system concluding a centrifugal separator.

By contrast, caustic soda produced by the IM-process is stronger and contains only a few p.p.m. of salt; therefore, the every compact falling-film evaporator can be employed. Moreover, the new system is designed to recover as much applied energy as possible, resulting in a dramatic reduction of the steam unit consumption to 0.4 tons per ton of NaOH.

2.7. *Performance of newest ion exchange membrane*

As already described, the performance of the IM-process has recently been much improved through technical developments and innovations including high performance ion exchange membranes, properly designed high grade anodes, activated cathodes with long life, implementation of zero gap electrolyser design and high quality brine supply. Table 2 gives the characteristics of four typical types of Japanese electrolyser. In addition, Figs 12 [13], 13 [12] and 14 [12] indicate the actual performance data.

The performance of each type of electrolyser has been summarized in Table 3. Precise com-

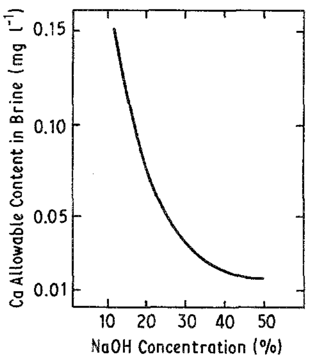

Fig. 11. Relation between calcium allowable content and NaOH concentration.

Table 2. *Characteristics of ion exchange membrane process electrolysers*

	Asahi Glass	*Asahi Chemical*	*Tokuyama Soda*	*Chlorine Engineers*
Name of process	AZEC	–	DN	CME
Cell type	Mono-polar	Bi-polar	Bi-polar	Mono-polar
Membrane–electrode gap	Zero gap	Zero gap	Zero gap	Narrow gap
Ion exchange membrane	FLEMION-DX		NEOSEPTA-F	
Exchange group	COONa 2-layer membrane	SO_3Na–COONa multi-layer membrane	SO_3Na–COONa multi-layer membrane	
Manufaturing process	Laminate	Surfacial chemical modification	Surfacial chemical modification	
Cathode side	COONa thin layer with low AR	COONa layer 5–12	COONa layer 10–20	
Anode side	COONa layer with high AR	SO_3Na layer	SO_3Na layer	
Exchange capacity	about 1.9 meq g^{-1}	about 0.8 meq g^{-1}	about 0.9 meq g^{-1}	
Membrane thickness (μm)	200–250	about 120	–	
Supporting material	Special micro pore fibre	Fluorofibre	Cloth	
Prevention of H_2 adhesion	Metal oxide porous layer	Coarse surface prepared at membrane manufacturing	Membrane surface treatment	
Effective area	$0.2\,m \times 1.0\,m = 0.2\,m^2$	$3.6\,m \times 1.5\,m = 5.4\,m^2$	$2.7\,m^2$	$3.03\,m^2$
Anode	Mesh-type DSA (flexible)	Solid solution of platinum group metal, valve metal, and oxygen	Mesh-type DSA	Mesh-type DSA
Cathode	Mesh-type soft steel with electrodeposited Ni and Raney Ni composite layer H_2 overvoltage: 0.12 V Performance: 3 years-on-line	Activated cathode of transition metal oxide with anti-reduction catalyst H_2 overvoltage: 0.15 V Performance: 3 years-on-line	LHOC Expandable soft steel with WC and Ni plating H_2 overvoltage: 0.1 V Performance: 5 years-on-line	Mesh-type stainless steel with activated catalyst powder and Ni-plating composite layer. H_2 overvoltage: 0.1 V Performance: 3 years-on-line
Commercial electrolyser				
Current (kA)	340	21.6	8.1	55
Current density (A dm^{-2})	31	40	30	30
Unit cell (No. per electrolyser)	552	80	90	6
Effective section area (dm^2)	0.2	5.4	2.7	3.0
Capacity (tons NaOH 100%/D)	11.6	59.4	24.8	1.89
Years-on-line	1	3	7	2

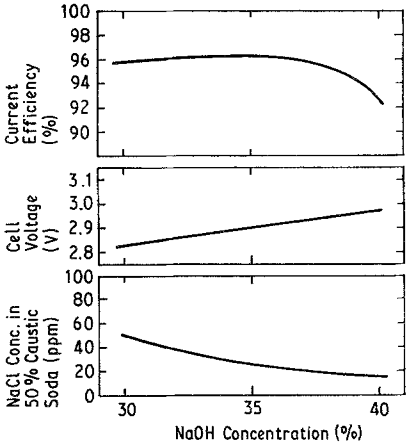

Fig. 12. Electrolysis performance of Flemion 755. NaCl concentration 200 g l^{-1} in anolyte; current density, 30 A dm^{-2}; temperature, 90° C.

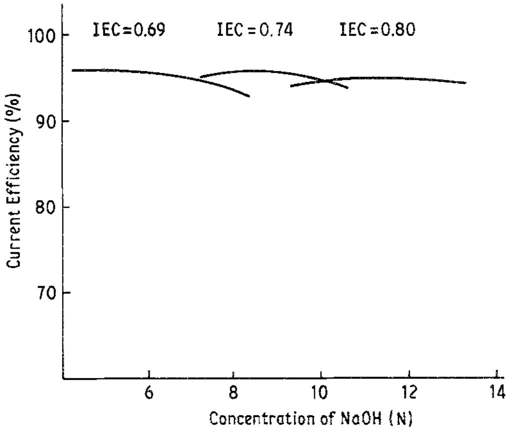

Fig. 13. Current efficiency versus NaOH concentration for multilayer perfluorocarboxylic and sulphonic acid membrane prepared by chemical treatment (COOH/SO_3H). IEC = ion exchange capacity (meq g^{-1} dry resin).

parison is not possible due to differences in design of the respective types of electrolyser; in general, however, the current efficiency reaches a level of almost 95% and the unit power consumption 2050–2100 kW h d.c. per ton of NaOH (100%). Taking into account the voltage drop over bus bars as well as the efficiency of current rectification, the practical unit power consumption is about 2200 kW h a.c. per ton of NaOH (100%).

3. ID-process/DI-process

The ion exchange membrane process which replaces the asbestos diaphragm of D-process cells with a cation exchange membrane has been developed and applied as a retrofitting process for the D-process cells. This improves the NaOH concentration in the catholyte from 12% with the D-process to 30–35%, resulting in a great reduction of unit steam consumption. In addition, the NaCl in the NaOH can be decreased to the level of the IM-process, eliminating the necessity to remove deposited salt as required in the D-process and so achieving considerable cost savings. The combined application of improved cathode configuration and activated cathodes reduces cell voltage appreciably which leads to energy savings of about 33% [14].

This process can be implemented with relatively little capital investment, requiring only the addition of a depleted brine line, dechlorination

Table 3. Membrane process data

	Asahi Glass	*Asahi Chemical*	*Tokuyama Soda*	*Chlorine Engineers*
Cell type	Mono-polar	Bi-polar	Bi-polar	Mono-polar
Current density (A dm^{-2})	30	40	40	30
Temperature (° C)	90	90	90	90
NaCl decomposition ratio (%)	50	70	–	50
NaOH concentration (%)	35	30	28	32
Cell voltage (V)	2.91	2.97	2.96	2.9†
Current efficiency (%)	95	95	95	95
Unit power consumption* (a.c. kW h per ton NaOH 100%)	2105	2148	2141	2098

* Current rectification efficiency: 97.5%.

† Excluding ohmic drop of inter-cell bus bars.

Table 4. Up-to-date data of ID/DI-process and HI-process

	Kanegafuchi Chemical Ind.	*Tokuyama Soda*	*Chlorine Engineers*	*Kanegafuchi Chemical Ind.*
Process name	ID-process	DI-process	DI-process	HI-process
Cell model	Hooker H-4 type	DS-85 type	MBC-29 type MBC-55 type	Mercury cell
Current (kA)	150	130	60 130	100
Number of cells	66	120	707	1
Capacity (tons per year)	120 000	180 000	697 200	
Membrane installation method	Cylindrical membrane inserted into cathode compartment box	Membrane bag enveloping anode	Membrane bag enveloping anode	Membrane horizontally attached to modified bottom plate
Years-on-line	4	1	3	1.5 (test cell)
Current density (A dm^{-2})	23.5	20	20.7 23.6	50
NaOH conc. (%)			32–35	
Temperature (°C)			90	
Cell voltage (V)	3.2	3.25	3.2–3.3	3.5
Current efficiency (%)		96	95–97	(95)
Unit power consumption (a.c. kW h per ton NaOH 100%)	2402	2315	Av. 2315	2520
Power		115	120	
Steam	134	120	Av. 115	
Total energy	2536	2550	Av. 2555	2520

Current rectification efficiency: 98%.
Steam-to-power conversion: 250 kW h t^{-1}.

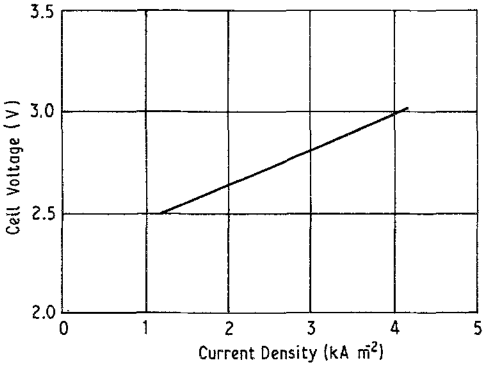

Fig. 14. Current density versus cell voltage with activated cathode.

system and secondary brine purification system to the existing D-process equipment besides partial modification of the electrolyser. This process, however, is suitable only for the modification of existing D-process plants and is therefore considered to be of transient value only. The technical performance from respective suppliers is summarized in Table 4.

4. HI-process

The HI-process, which is still under development for commercial use, is a conversion to the membrane process for M-process cells having relatively small current density. In the HI-process the ion exchange membrane is horizontally stretched on the modified bottom plate of the M-process cells, NaOH solution is force-circulated to the cathode compartment in the minute gap between the membrane and the bottom plate and electrolysis is carried out without H_2 blinding. Since this process requires almost no modification of the electrolysis facilities of the M-process, the capital investment is small; however, the current density is limited to a maximum of 50 A dm^{-2} and so if this process is applied to M-process cells normally operating at 100–120 A cm^{-2} the production capacity is naturally halved.

The performance data is given in Table 4. This process is also considered to be a transient process prior to installation of the IM-process. The configuration of the HI-process is shown in Fig. 15.

5. Capital investment for conversion

So far the technical aspects of the membrane process have been discussed. Also important in determining the conversion programme is the cost. The capital investment required for the conversion is largely governed by the nature of the conversion and plant capacity and has to be decided in relation to market demand. Generalizations may not always apply.

When the M-process is converted to the IM-process, modification of the primary brine purification system and addition of the secondary brine purification, electrolytic cell, evaporator, etc. are necessary. In some cases modification or replacement of the rectifier may also be required. For the D-process, addition of the depleted brine lines for brine circulation is necessary; however, the evaporation system can be adapted. When the D-process is converted into the DI-process, the addition of a depleted brine line and the secondary brine purification

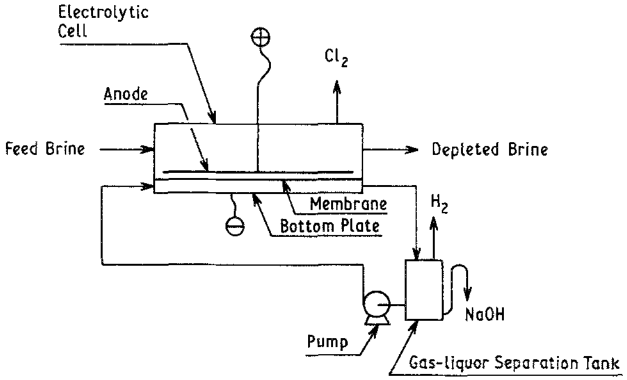

Fig. 15. HI-process electrolyser.

Table 5. Capital investment required for process conversion and energy savings effect

	M → IM-process *D → IM-process*	*D → DI-process* *M → HI-process*	*Average of all converted plants in Japan*
Investment (Plant capacity 1000 tons per month as NaOH)	US\$2.25 million	US\$1.08 million	US\$1.87 million
Energy saving ratio (power kW h)	(D → IM-process) 40–44%	(D → DI-process) 20–32%	

Steam-to-power conversion: 250 kW h t^{-1} (see Table 4).

system are required as well as modification of the cells and a sulphate removal system. For the conversion from the M-process to the HI-process, modification of the primary brine purification system and of the electrolytic cells, and additional installation of a secondary brine purification system and an evaporator are required.

The capital investment can be classified by the pattern of the conversion. As mentioned above, the actual conversion cost is difficult to estimate; however, the data from MITI is summarized in Table 5 [2]. According to the data the conversion from the M-process or the D-process to the IM-process needs some 540 million yen per 1000 tons per month of NaOH, while from the D-process to the DI-process, or from the M-process to the HI-process need some 260 million yen per 1000 tons per month of NaOH.

From the above estimate, the DI-process or the HI-process can be implemented at half the capital investment required for conversion from the M-process or D-process systems. In view of the low energy savings, however, the effect of investment after depreciation is considered to be reversed.

6. Licensing of Japanese process techniques

As described earlier in this article, Japanese membrane cell technology has undergone various stages of development and improvement before its acceptance as established industrial technology. At the time of writing, many mem-

Table 6. Asahi Glass process

Customer	*Place*	*Plant capacity (tons per year NaOH)*	*Start-up*
Asahi Glass	Osaka	10 000	1978
Nippon Carbide Ind.	Toyama	18 000	1980
Thai Asahi Caustic Soda	Bangkok (Thailand)	14 400	1981
Tsurumi Soda	Kanagawa	12 000	1982
Kashima Chlor-alkali (1st period)	Ibaragi	115 500	1983
Nankai Chemical	Kochi	14 400	1983
Kansai Chlor-alkali	Osaka	40 000	1984
Kashima Chlor-alkali (2nd period)	Ibaragi	148 000	1984
Giho Chemical	Taipei (Taiwan)	18 000	1984
Egypt Petrochemical	Alexandria (Egypt)	66 000	1985
Thai Asahi Caustic Soda	Bangkok (Thailand)	10 000	1985
Central Chemical	Kanagawa	55 000	1985
Tengen Chemical	Shanghai (China)	10 000	1986
Total		531 300	

Table 7. Asahi Chemical process

Company	*Location*	*Plant capacity (tons per year NaOH)*	*Start-up*
Asahi Chemical Ind. Co., Ltd	Nobeoka, Japan	40 000	1975
Denki Kagaku Kogyo K. K.	Ohmi, Japan	60 000	1976
Asahi Chemical Ind. Co., Ltd	Nobeoka, Japan	40 000	1977
Prince Albert Pulp Co., Ltd	Saskatoon, Canada	30 000	1978
St. Anne Chemical Co., Ltd	Nackawic, Canada	10 000	1979
N.Z. Forest Products Ltd	Kinleith, New Zealand	10 000	1981
Asahi Chemical Ind. Co., Ltd	Nobeoka, Japan	40 000	1982
Tasman Pulp and Paper Co., Ltd	Kawarau, New Zealand	10 000	1982
Akzo Zout Chemie Nederland b.v.	Rotterdam, Netherlands	280 000	1983
Kikkei Kako Co., Ltd	Kambara, Japan	36 000	1984
Kureha Chemical Ind. Co., Ltd	Nishiki, Japan	96 000	1985
Lanzhow Chemical Corporation	Lanzhow, China	10 000	1985
Qiqihar Electrochemical Co.	Qiqihar, China	10 000	1986
Total		672 000	

brane process plants are in service or under construction. The situation with regard to the licensing of Japanese technology is summarized in Tables 6–10. Conversion to membrane process plants seems to be a world trend.

7. Future prospects

7.1. *IM-process*

As described earlier, the performance of the IM-process has been greatly enhanced and the number of plants applying this process are increasing. However, present ion exchange membranes are not yet ideal and efforts to develop membranes having lower electrical resistance and higher current efficiency continue. In future, membranes will be available with a performance designed to meet the general specifications of the customer. Custom-made membranes to meet the operating conditions of the user, e.g. large flexibility in load variation, need for decreasing oxygen in chlorine and minimizing salt in caustic soda will be available in addition to those of standard performance.

While the present caustic soda concentration produced directly by commercial cells is not more than 35%, levels close to 50% will be produced economically in the future; in such cases, however, materials for electrolyser hardware will have to be reviewed.

The operating technology of the IM-process is certain to become more sophisticated with intensive instrumentation and computerized operation.

Table 8. Tokuyama Soda process

Company	*Location*	*Plant capacity (tons per year NaOH)*	*Start-up*
Tokuyama Soda	Tokuyama	10 000	1977
Kanegafuchi Chemical Ind.	Takasago	120 000 (membrane supply only)	1981
Kokuto Chemical	Korea	3 600	1981
PIC	Kuwait	36 000	1982
FPC	Taiwan	10 000	1984
Total		179 600	

Table 9. Chlorine Engineers process (CME)

Company	*Location*	*Plant capacity (tons per year NaOH)*	*Start-up*
Showa Enso	Okinawa	2 800	1980
Mitsui Toatsu Chemical	Ohmuta	5 800	1983
Mitsui Toatsu Chemical	Nagoya	5 800	1984
Mitsui Toatsu Chemical	Osaka	55 200	1984
Nippon Soda	Takaoka	54 000	1985
Toagosei Chemical Industry	Nagoya	72 000	1985
Osaka Soda	Kokura	30 000	1985
Confidential		7 700	1986
Total		233 300	

It is noteworthy that (in July 1985) Asahi Chemical and Asahi Glass jointly established a new company, Asahi IM Engineering, based on a condition of patent dispute conciliation.

7.2. *DI-process and HI-process*

These processes are designed to convert existing D-process cells or M-process cells operating at relatively small current densities into membrane process cells for a relatively low investment. Although they have many unique advantages, the installation of a new IM-process plant will be required when the electrolyser becomes old.

7.3. *Solid polymer electrolyte (SPE) process*

The SPE is a unique technology and may be regarded as the basis for electrolysers of the future. Initially, it was developed as water electrolysis technology for space exploration by General Electric Company, USA. Later, De Nora, Italy, succeeded in the development for the application to brine electrolysis. Several difficulties were overcome and favourable results were achieved. However, there are points yet to be solved before commercial application, i.e. economy derived from the cell life governed by the shortest integral constituents of membrane,

Table 10. DI-process

Customer	*Location*	*Plant capacity (tons per year NaOH)*	*Start-up*	*Process owner*
Kanegafuchi Chemical Ind.	Takasago	120 000	1981	Kanegafuchi Chemical Ind.
Tokuyama Soda	Tokuyama	203 000	1983	Chlorine Engineers
Mitsui Toatsu Chemical	Nagoya	64 000	1983	Chlorine Engineers
Toyo Soda	Yokkaichi	71 000	1984	Chlorine Engineers
Mitsui Toatsu	Ohmuta	68 000	1984	Chlorine Engineers
Hodogaya Chemical	Koriyama	38 000	1984	Chlorine Engineers
Osaka Soda	Matsuyama	37 000	1984	Chlorine Engineers
Toagosei Chemical Ind.	Tokushima	35 000	1984	Chlorine Engineers
Kanto Denka Kogyo	Mizushima	53 000	1984	Chlorine Engineers
Sumitomo Chemical	Ohita	14 000	1984	Chlorine Engineers
Nipon Enka Vinyl	Chiba	87 000	1985	Chlorine Engineers
Ajinomoto	Kanagawa	37 000	1985	Chlorine Engineers
Total		827 000		

anode and cathode, expensive noble metal catalyst and high manufacturing cost of the current collector.

Although the advantage of the SPE process seems to be partially realized by the no-gap IM-process, the SPE process is still considered to play an important role in the progress of electrolysis technology.

7.4. *Oxygen cathode process*

The oxygen cathode process has been developed as a means of reducing energy consumption. In this process, hydrogen gas is not evolved but reacts with oxygen to form water so that voltage can theoretically be reduced by about 1.2 V. The technology uses a gas dispersion electrode for the cathode. The applied cathode is prepared in such a way that carbon powder impregnated with catalyst metal is coated on a metal screen or sintered porous nickel substrate using a Teflon binder. Therefore reaction occurs at the three-phase interfaces, electrolyte–catalyst–reaction gas, in which the balance between liquid pressure and gas pressure is a key factor. Other important subjects for development include selection of proper catalyst, prolongation of catalyst life, improvement of corrosion resistance of carbon support, economical removal of CO_2, or moisturing when air is applied for oxidation [17, 18]. As an electode for commercial cells, it must be a highly activated cathode with at least 1 m^2 of electrode area, of uniform activity and with more than one year of life. Consideration should also be given to safety in case of decreased activity.

Hydrogen is widely used for hydrochloric acid synthesis, hydrogenation processes as a petrochemical feedstock and as high purity hydrogen. Therefore when evaluating the cost effectiveness of the oxygen cathode it must be realized that if no hydrogen is generated, alternative means of hydrogen production may be required.

Judging from the above, the practical application of the oxygen cathode process may be well into the future.

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