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Modification of diaphragm-type chlor-alkali cells to ion exchange membrane cells

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Ion exchange membrane cell technology, recently developed for producing chlorine and caustic soda, has been applied to the modification of existing diaphragm cells into special IEM cells, termed the MBC®, which offer a higher energy (electricity and steam) efficiency and a higher product quality than those of diaphragm cells with only a small amount of additional modification cost.

1. Introduction

Ion exchange membrane (IEM) process technology has advanced rapidly over the last ten years in the chlor-alkali field, especially in Japan, as a pollution-free process for producing high quality caustic soda [1, 2]. It is also recognized that the IEM process is the most energy (both electricity and steam) efficient as compared to the conventional amalgam and diaphragm processes [3]. Electrochemical theory regarding both diagram and IEM cells is similar but IEM cells produce concentrated caustic soda in the range 32–35%, almost free from NaCl, compared to the cell liquor (mixture of NaCl: $190\,\mathrm{g\,l^{-1}}$ and NaOH: $130\,\mathrm{g\,l^{-1}}$) produced in diaphragm cells. This is due to the different separator material in the cells. It may be asked whether these new IEM cells are introduced to replace diaphragm cells or if diaphragm cells can be modified to become special IEM cells because of the similarity between them [4].

In fact, the technology to modify diaphragm cells into special IEM cells has been developed and applied to 12 diaphragm cell plants. The total capacity of these modified plants is some 58 000 tons per month of NaOH on a 100% basis [5]. Fig. 1 illustrates an example of the flow sheet in the modification of a chlor-alkali plant from the diaphragm process to the IEM process.

2. The feasibility of modification of the diaphragm process plant

The diaphragm process plant can be modified easily and economically to the IEM process plant for the following reasons:

(i) Almost all the brine treatment facility is utilized for the process change. Only an ion-exchange resin column has to be installed to polish the filtered brine prior to sending it to the IEM cell; this is termed secondary brine purification [6].

(ii) Complete dechlorination of the depleted brine is required to prevent degradation of the ion exchange resin in the secondary brine purification system. Chlorine is recovered from the brine by vacuum and/or aeration, followed by chemical reduction, before returning it to the salt saturation stage.

(iii) Circulation of the catholyte between the cell and the reservoir is necessary to adjust and control the solution concentration and temperature.

(iv) The evaporator is utilized with minor changes because the IEM cell caustic liquor is free of salt and is more highly concentrated than the diaphragm cell caustic liquor. The steam consumption for evaporation is thus reduced significantly and troubles with erosion-corrosion caused by salt slurry are minimized.

With these concepts in mind, the modification of diaphragm cells into IEM cells, and that of the flow sheet, have been investigated in detail from both technological and economic standpoints.

3. Basic concept of the cell modification

The hardware design of diaphragm cells such as the Hooker H and the Diamond Shamrock MDC has been optimized through the accumulated experience of many years in practical plants [7]. This is particularly true of the anode and cathode structures. Therefore, the anode and the cathode have to be utilized with minor modifications to save extra expense. Asbestos fibre is normally vacuum-deposited on the cathode screen of the diaphragm cell. However, in the cell modification the ion exchange membrane fabricated in the form of a bag is mounted on the DSA® anodes rather than on the cathode for ease of installation and servicing. The procedure for fabricating the membrane bag was established to ensure good performance by the modified cell at minimum cost.

4. Tests and results

4.1. *Fabrication of the membrane bag*

As any leakage of the electrolyte through the membrane bag for many thousands of hours cannot be tolerated, bonding is all-important and an attempt was made to bond Nafion® [8] 900's by heat sealing.

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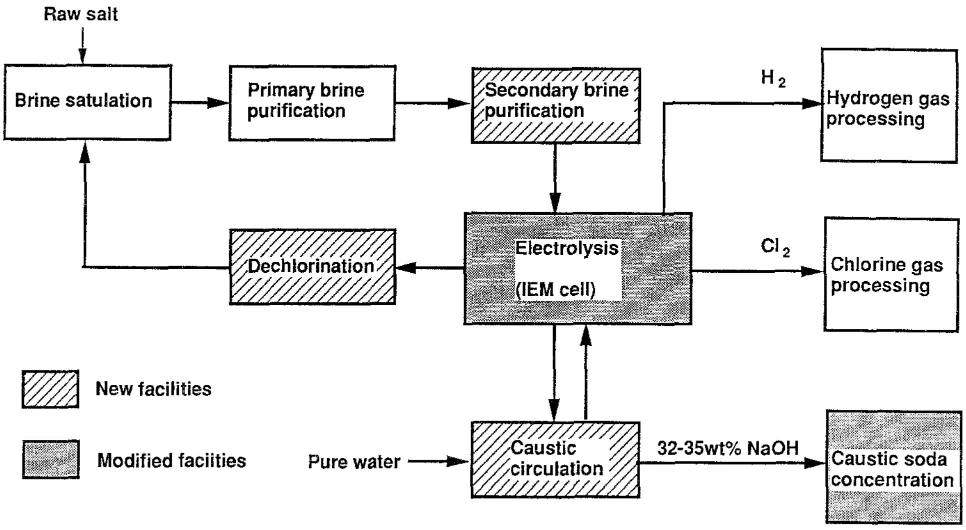

Fig. 1. Typical process flow in the modification from diaphragm process to membrane process.

However, this proved impossible because Nafion® 900 series consists of sulphonate polymer on the anode side and carboxylate polymer on the cathode side, while the glass transition points of these polymers differ.

Next, two strips of a sulphonate polymer membrane reinforced with Teflon® cloth (standard Nafion®) were located on both sides of the membrane as shown in Fig. 2, then heated to a certain temperature under pressure and left for a while. The strips were bonded satisfactorily with both polymers of the membrane. Temperature, pressure, and holding time under such conditions are three key factors for the bonding of the membrane and each factor must be investigated through trials to find the most suitable integrated bonding conditions and specification for the objects to be bonded (type of membrane, number of sheets, straight line or corner, etc.). Table 1 shows an example of fabricated condiditons. The physicochemical properties of the strip are of great importance.

A number of 10 mm × 140 mm specimens were prepared for examining the bonding strength. Also the membrane bag was cut to obtain a 10 mm × 140 mm test specimen after electrolysis for 90 days under the same conditions as those of the practical cell. The test specimens were immersed in pure water at room temperature for one hour, removed, and then measured in the wet state for tensile strength under the conditions of: load = 50 kg, speed = 50 mm s^{-1}, at room temperature. All the specimens tested failed in the bulk polymer but not at the bonded area nor near it. Table 2 indicates that the tensile strength of the bonded membranes is almost the same as that of the virgin Nafion®, and that the bonding strength is unaffected by electrolysis. Consequently, the procedure outlined in Table 1 was applied to fabricate the membrane bag.

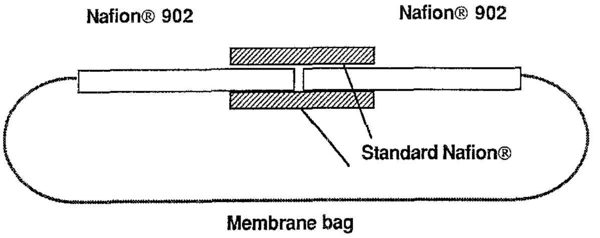

Fig. 2. Heat seal of the membrane.

4.2. *Self-circulation of anolyte*

Since the membrane bag is mounted on the anode box, chlorine bubbles pass through the holes of the anode mesh, and the gas-solution mixture ascends the anode. Gas bubbles must be removed from the anode surface since, otherwise, the overvoltage increases greatly due to the decrease of the effective area of the anode.

A solution downcomer was provided in the anode box by utilizing the existing anode spring and an additional back-up spring to stimulate the solution circulation as shown in Fig. 3. The solution leaves gas bubbles at the cell top and descends through the solution downcomer to the botton by gravity, and hence the anolyte is circulated in the anode structure without being pumped. As a result of the preliminary experiment with a pilot cell, the brine flow was found to be stimulated extensively by this method, and its volumetric flow rate was measured at 20 times the flow rate of feed brine. As a result, gas release from the anode and the anolyte was enhanced and gas void fraction decreased.

Twenty three membrane bags were positioned between the cathode tubes of the cathode box and each of these bags was connected with the manifold by two tubes, an up-flow tube and a down-flow tube, as shown in Fig. 3. Therefore the secondary self-

Table 1. Fabrication conditions of membrane bag

Membrane	Nafion® 902
Strip	Sulphonate polymer membrane reinforced with Teflon® cloth (standard Nafion®)
Heat temperature	200–250° C
Pressure	3–4 kg cm^{-2}
Holding time	0.5–1.5 min

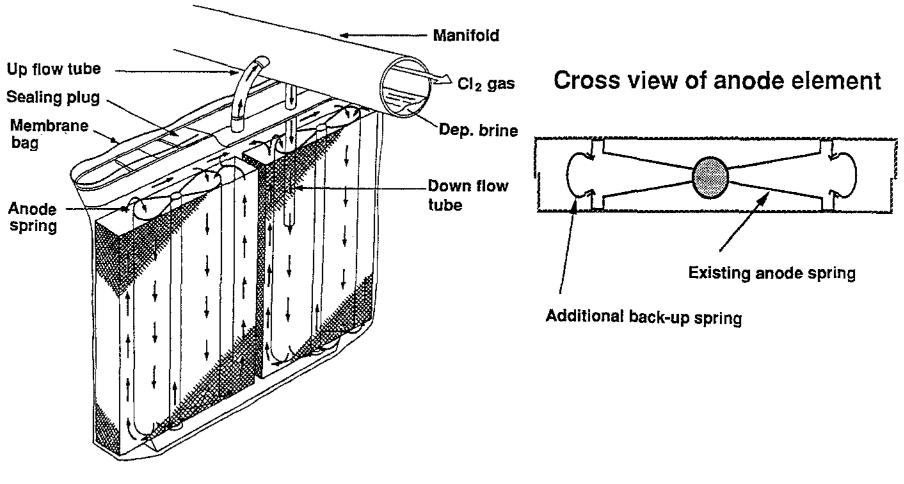

Fig. 3. Flow pattern of the self-circulation of anolyte in the anode compartment formed by the membrane bag and the manifold.

circulation of the anolyte between the manifold and each of these bags occurred automatically due to the difference in specific gravity of the anolyte in the tubes (up-flow tube: mixture of gas and liquor, down-flow tube: liquor only). Hence the depleted brine and chlorine gas were easily taken from the membrane bags to the manifold and the feed brine charged to the manifold was smoothly introduced into the membrane bags together with the circulating anolyte. Uniform distribution of the NaCl concentration along the anode and the membrane bags was also achieved in the range of 200–210 $g\,l^{-1}$. All these effects, stemming from the two anolyte self-circulations and effective gas lift in the anode compartment formed by the membrane bag, are required to keep the cell performance high.

4.3. *Cathode structure*

The cathode tube in modern diaphragm cells is fabricated with carbon steel mesh or perforated steel plate, and extends from side to side all the way across the cathode box, as shown in Fig. 4. There is a space around the box where hydrogen and caustic liquor enter. Although fibrous asbestos is deposited on the cathode of the diaphragm cell under vacuum, the cathode in the modified cell is not covered, and is utilized in that condition without renovation. Since there are spaces between the cathode tube and the membrane, as well as at both ends of the cathode tubes, some of the catholyte flows from top to bottom of the cathode compartment after it has discharged hydrogen bubbles. Thus, circulation of the solution along the cathode tubes and their end spaces is established, as shown in Fig. 4, resulting in uniform concentration of caustic soda solution throughout the cathode box (see Fig. 5).

Table 2. Results of tensile strength tests

Virgin Nafion® 902	4.0 $kg\,cm^{-1}$
Test specimen	
Before electrolysis	3.9 $kg\,cm^{-1}$
After electrolysis	3.7 $kg\,cm^{-1}$

4.4. *Structure of membrane bag cell*

The diaphragm cell has been modified to the IEM cell equipped with a membrane bag instead of a sheet. Therefore, the modified cell is named 'Membrane Bag Cell' or in short MBC®. The MBC® has been developed through extensive trials, innovation, experiments, and tests in both laboratory and practical plant. The membrane bag and the mechanical seal with the cell cover are examples.

The MBC® has two models: Type A and Type B as shown in Figs 6 and 7, respectively. Type A utilizes the existing cell cover of the diaphragm cell with minor modification, and is desirable when the cell can be installed in the outside of the cell room. On the other hand, Type B is equipped with a new cover that has manifolds for distributing the feed brine and discharging the depleted brine and chlorine gas; thus it replaces the original diaphragm cell cover.

Control of the pressure balance of the anode-membrane in the cell structure is an important operational factor. Therefore, a butterfly valve was mounted on the hydrogen gas outlet nozzle (see Figs 6 and 7), and the pressure of the gas was controlled at a slightly higher rate than that of the anolyte to keep the membrane bag securely mounted on the anode.

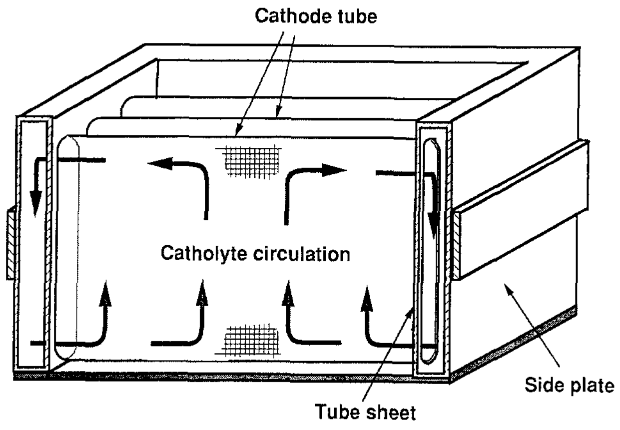

Fig. 4. Flow pattern of the self-circulation of catholyte in the cathode box.

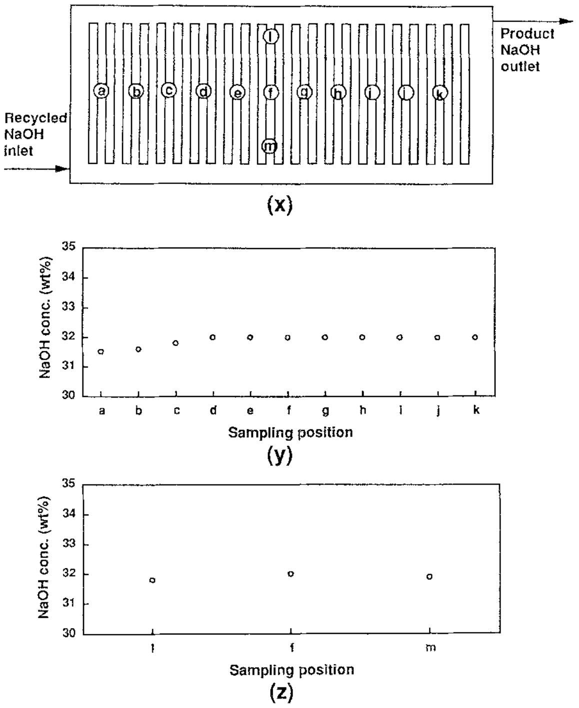

Fig. 5. Distribution of caustic soda concentration in the cathode box.

Table 3. Specification of MBC-29B

Cell type	MBC-29B
Rated current	60 kA
Rated current density	2.07 kA m^{-2}
Number of anodes	2 × 23 = 46 blades
Anode effective area	29 m^2
Number of IEM bags	23 bags (two anode blades in one bag)
Membrane	Nafion® 902
Cathode	Activated cathode coating

4.5. *Results and performance of the MBC® cells*

The Diamond Shamrock MDC-29 cell has been reformed as the membrane bag cell, named MBC-29B. Table 3 shows the design specifications of MBC-29B. This cell has been operated successfully in a plant since 1982, and an example of its performance is illustrated in Fig. 8. The cell voltage has gradually increased from 3.3 to 3.4 V at a current density of 2.07 kA m^{-2} as shown in the top graph of Fig. 8, and the current efficiency has gradually decreased with time (second graph in Fig. 8). As a result, the electric power consumption per ton of caustic soda has gradually increased to 2 450 kWh from 2 300 kWh and also the NaCl content in the product caustic soda shows a similar progress from 20 to 40 ppm as shown in the third and last graphs of Fig. 8, respectively. The membrane bag will be replaced in about 3–3½ years for economic reasons (higher power consumption or higher NaCl content in the product caustic soda). Any membrane bag damaged during assembly work or operation can be dismounted from the cell, and then repaired by the same technology as for bag fabrication.

Table 4 shows the comparison of specifications, performances, and product quality of cells MDC-29 and MDC-29B respectively, before and after modification. By weight the catholyte liquor of MBC® is about 32–35% concentrated caustic soda, almost free from NaCl. Consequently, the steam requirement for concentrating it to a marketable 50% caustic liquor is only 0.4–0.6 t/100% NaOH compared to 2.6–2.8 tons for diaphragm-cell caustic soda.

It is well known that the diaphragm cell is sensitive to fluctuations of current load and brine flow, and hence its operation is troublesome when the electric power supply is insufficient. On the other hand, the membrane cell is unaffected by a wide-ranging current change, that is, the cell can respond to fluctuations of load in a relatively short period. This means that off-peak electricity can be utilized cheaply with a small additional charge and a little extra labour for the process change. It is one of the attractive points of the membrane cell process, especially in Japan where energy is expensive.

The cathode of the IEM cell is normally coated with active material to reduce the hydrogen overvoltage, thus achieving a cell voltage saving of some 0.2 V. Since the cathode of a diaphragm cell is normally covered with asbestos mat, the caustic con-

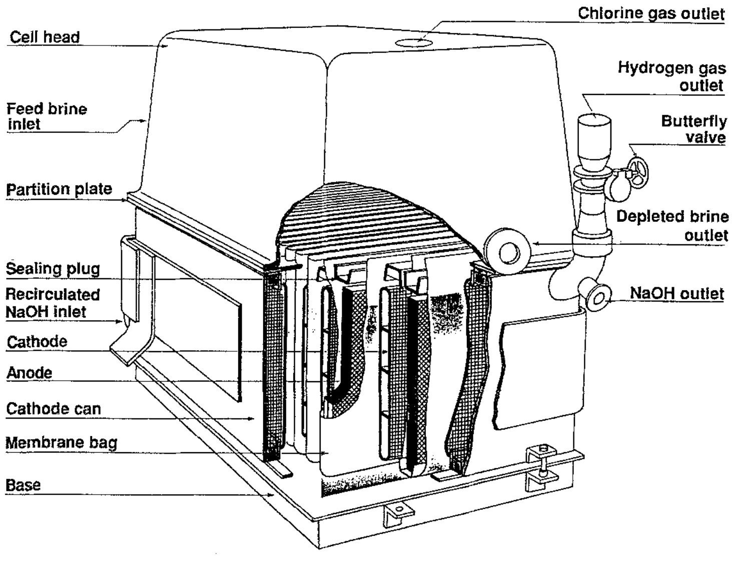

Fig. 6. MBC® cell structure (A Type).

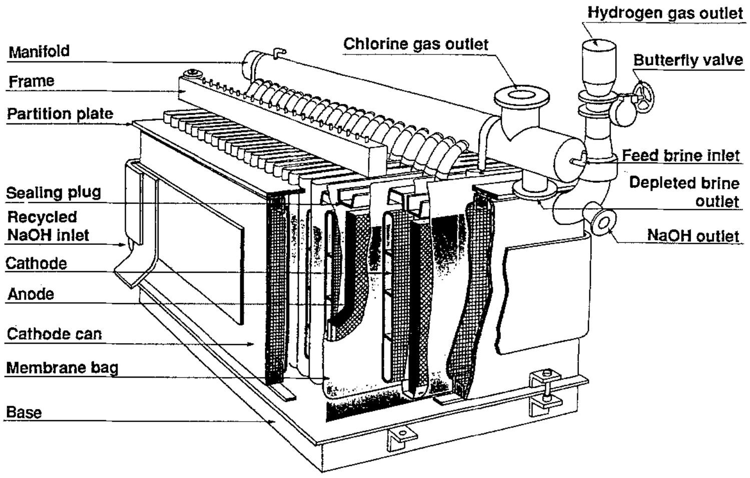

Fig. 7. MBC® cell structure (B Type).

centration on the cathode surface is higher than that in the bulk of the catholyte due to mass transfer limitations, and the cathode coating is attacked or deactivated in a relatively short period. On the other hand, the cathode of the MBC® is separated from the membrane, and the catholyte-hydrogen mixture ascends into this space, resulting in uniform caustic soda concentration and temperature. Consequently, a prolonged life at the activated cathode in the MBC® is assured even if the caustic concentration in the bulk is higher than that in a diaphragm cell (see Table 4). A number of Type A cells are also working under similar conditions and with similar performances as Type B.

5. Conclusion

It is now evident that the membrane process has a number of advantages in comparison with the conventional diaphragm process, although it requires extra pure brine as feed since otherwise expensive membranes are damaged. Combining the technologies of the membrane process and the diaphragm process, modification of the existing cells to the special membrane bag cells (MBC®) has been conducted. Oxide coated titanium anodes or DSA® were covered with the membrane bag and fixed to the cell base. The cathode box of the diaphragm cell was utilized without any renovation. The modified cell, MBC®,

Table 4. Performance comparison between membrane bag cell and the mother diaphragm cell

Name	*Membrane bag cell MBC-29*	*Diaphragm cell MDC-29*
Current load (kA)	60	60
Current density ($\mathrm{kA\,m^{-2}}$)	2.07	2.07
Production, NaOH (T/D)	2.07	2.05
Separators	Nafion® 902	Modified asbestos diaphragm
Anodes	DSA® (modified)	DSA® (expandable)
Cathodes	Activated coating on mild steel mesh	Mild steel mesh
Cell voltage (V)	3.25–3.30	3.30–3.35
Current efficiency (%)	96–97	95–96
Power consumption ($\mathrm{kWh\,t^{-1}}$-NaOH)	2,245–2,300	2,300–2,360
Cell liquor		
NaOH	32%	130 $\mathrm{g\,l^{-1}}$
NaCl	40–60 ppm	190 $\mathrm{g\,l^{-1}}$
Feed brine		
Flow rate ($\mathrm{m^3\,hr^{-1}}$)	1.0	0.85
NaCl ($\mathrm{g\,l^{-1}}$)	300–305	310–320
Hardness (Ca + Mg)	25 ppb	8 ppm
Depleted brine		
NaCl ($\mathrm{g\,l^{-1}}$)	200–210	180–190 (discharged as cell liquor)
Depletion ratio of NaCl (%)	42	50
Chlorine gas		
Cl_2 (vol %)	98–99	97–98
O_2 (vol %)	1.5–2.0	2.0–2.5
Hydrogen gas		
H_2 (vol %)	99.9	99.9
Operating temp (°C)	90	90

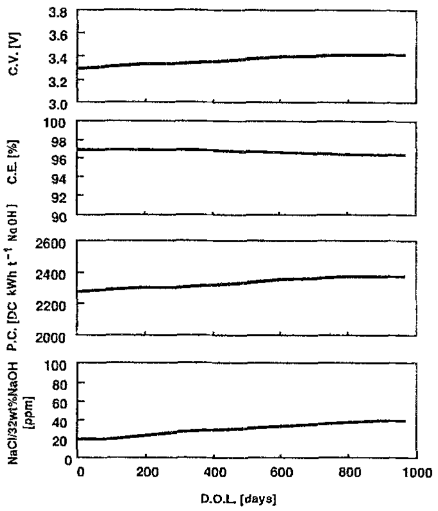

Fig. 8. Typical cell performance of MBC-29B, equipped with Nafion® 902, DSA® and an activated cathode. Operating conditions: current density = 2.07 kA m^{-2}, operating temp. = 90° C, NaOH conc. = 32 wt %.

showed superior results and performances in both experimental stations and practical plant. About 700 MBC® cells are being operated at 12 plants producing high quality caustic soda with minimum energy consumption. The total production of these cells is some 58 000 metric tons of caustic soda per month, or 22% of the total installed membrane cell capacity in Japan.

Acknowledgements

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[8] Nafion® is the registered trademark of E. I. du Pont de Nemours and Company for its Nafion® perfluorinated products.