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## 3 The chlor-alkali industry

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The electrolysis of aqueous sodium chloride, normally brine obtained directly from natural salt deposits, to yield chlorine, sodium hydroxide and hydrogen is the largest of the electrolytic industries. In 1986, the world's annual production of chlorine was a little under  $3.5 \times 10^7$  ton. The USA was the largest producer at 10.4 million ton, followed by Western Europe (9.5 million ton), and Japan (3 million ton).

The electrode reactions are, at the anode:



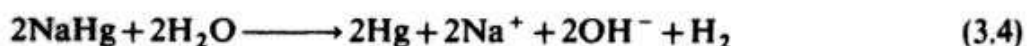
and at the cathode either, directly:



or indirectly as in a mercury cell where the cathode reaction is:



and the sodium amalgam is decomposed in a separate reactor to give the desired products:



Both chlorine and sodium hydroxide (normally traded as a 50%w/v aqueous solution) must be considered to be main products; the one in greater demand varies with time. Their major uses are summarized in Table 3.1. The hydrogen is also used, where possible, as a chemical (e.g. for the hydrogenation of fats), otherwise as a fuel (e.g. at the power station which is inevitably on site at any large chlor-alkali facility).

The chlor-alkali industry should be particularly interesting to the student of electrochemical technology. Firstly, it is by any standards, a process carried out on a very large scale and at many sites and it is central to the chemical industry as a whole. In addition, three different electrolytic technologies based on mercury, diaphragm and membrane cells are all currently used. Moreover,

although it is a mature industry – the first electrolytic cells having been introduced in the 1890s – the last 25 years have seen extensive and notable advances in the technology resulting both from scientific innovation and the economic and social pressure for energy conservation, pollution control and higher safety standards. In consequence, we shall see that membrane-cell technology, almost unknown in 1970, has advanced to the point where it is increasingly considered superior in performance. In 1987, it was responsible for about 10% of the total world production and by the year 2000, it is expected to be the dominant, and perhaps the only, technology within the chlor-alkali industry.

The majority of the chlorine produced is used internally within the chemical industry for the manufacture of polyvinyl chloride, chlorinated hydrocarbons, propylene oxide, etc. (Table 3.1). Hence, it is common to find chlor-alkali plants as part of very large, integrated chemical complexes and the capacity of such plants may be  $0.5 \times 10^6$  tons  $\text{Cl}_2$ /year. On the other hand, concern about the transport and storage of liquid chlorine has led to a different trend towards smaller plants sited close to the user. This is particularly attractive when there is an almost balanced requirement for both chlorine and sodium hydroxide, e.g. in pulp and paper mills (Table 3.1). A typical plant in this application may have a capacity of  $10^4$  tons  $\text{Cl}_2$ /year. On an even smaller scale, the same concerns lead to a need for plants, for example, to provide  $\text{Cl}_2$  to prevent biological growth on

**Table 3.1** Major uses of chlorine and sodium hydroxide\*

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Chlorine:	
Manufacture of polyvinylchloride	(20)
Preparation of chlorinated organic solvents, e.g. methylene chloride, chloroform, carbon tetrachloride, <i>per</i> - and <i>tri</i> -chloroethylene, 1,1,1- <i>tri</i> -chloroethane	(26)
Preparation of propylene oxide	(8)
Synthesis of other organic compounds, e.g. chlorobenzenes, alkyl chlorides (particularly methyl chloride for lead alkyls), herbicides	(7)
Preparation of fluorocarbons	(4)
Pulp and paper manufacture	(14)
Preparation of inorganic compounds, e.g. sodium hypochlorite, titanium tetrachloride, iodine chlorides	(12)
Water treatment	(4)
Sodium hydroxide (Caustic soda):	
Synthesis of many organic compounds	(38)
Manufacture of textiles and rayon	(5)
Soap and detergent production	(5)
Oil refining	(5)
Paper and pump manufacture	(20)
Aluminium extraction	(4)
Manufacture of inorganic compounds, e.g. sodium cyanide, sodium salts	(11)

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\* Figures in brackets are percentages of US production (taken from E. Spore and B. V. Tilak (1987) *J. Electrochem. Soc.*, 134, 179c.

water-intake pipes at power stations or to service a single swimming pool (0.1–10 tons Cl<sub>2</sub>/year). Clearly, there is great diversity in the size of plant demanded by customers. The markets may be met either by purpose-built units for each application or using a modular concept where cell units can be built together to give the required capacity. Both approaches have been used. In this chapter, however, emphasis is placed on the discussion of the larger-scale plants.

### 3.1 GENERAL CONCEPTS OF BRINE ELECTROLYSIS

A discussion of the electrolytic production of chlorine and sodium hydroxide requires an understanding of the very large scale of the industry. The annual world production of chlorine was noted above as  $3.5 \times 10^7$  tons. It is difficult to comprehend the enormity of this scale but it can be put into different terms, e.g. this chlorine production rate requires some 2 km<sup>2</sup> (or almost a square mile) of anode and the consumption of 10<sup>8</sup> MWh of electricity (say 1–2% of the electricity generated or the output of more than ten very large power stations). Even in the absence of a discussion of the economics of the process, it can be seen that we are dealing with an energy-intensive process requiring many cell units. Therefore, we shall be looking for:

1. Simple and cheap cell design.
2. High current densities to minimize capital investment in plant.
3. Cell components which are reliable, readily available and have a long lifetime, so as to minimize downtime.
4. Good current efficiency and material yields for both the anode and cathode reactions. Parasitic reactions not only lower the energy consumption and increase the use of materials but also lead to impurities in the products.
5. Low power consumption (kWh ton<sup>-1</sup>). This is determined by the current efficiency and the cell voltage. The latter was discussed in Chapter 2 and it was shown that the cell voltage is made up of a number of terms, i.e.:

$$E_{\text{CELL}} = E_c^C - E_c^A - |\eta_A| - |\eta_C| - iR_{\text{CELL}} - iR_{\text{CIRCUIT}} \quad (3.5)$$

and good energy efficiency will be obtained only if attention is paid to minimizing each component voltage.

Table 3.2 lists the equilibrium potentials for the four electrode reactions which must be considered in brine electrolysis. The data are given for 25% brine and at pH values important to an understanding of the chemistry of a chlor-alkali cell. Even so, the data do not correspond to the exact conditions of industrial cells, since activity coefficients have been assumed to be 1 and the values are presented for room temperature and pressure. In fact, slightly elevated temperatures and pressures, 60–95°C and 1–10 atm. respectively would be more normal. But the equilibrium potentials in Table 3.2 form a sensible basis for discussing the cell chemistry.

Chloride ion is usually oxidized in a slightly acid solution to prevent hydrolysis of the chlorine to hypochlorite and also to minimize the oxygen evolved in competing water oxidation at the anode. The pH at the cathode in a diaphragm and membrane cell will be about 14 as the electrode reaction generates hydroxide. Two factors emerge immediately:

1. In a mercury cell, where the electrode reactions are A and D in Table 3.2, the term  $(E_e^C - E_e^A)$  of equation (3.5) is  $-3.16$  V, a value much larger than the corresponding minimum cell voltage for a diaphragm or membrane cell,  $-2.15$  V, where the electrode reactions are A and C(ii). Hence, a mercury cell is only competitive because some other terms in equation (3.5) are favourable, e.g. a mercury cell does not require a separator between the electrodes and, hence,  $R_{\text{CELL}}$  is lower.
2. The potential advantage of a membrane cell with an oxygen cathode, i.e. a cell where the reactions are A and B(ii), can readily be seen. The equilibrium cell voltage is reduced to  $-0.92$  V.

It can also be seen that kinetics play an important role in a chlor-alkali cell. A mercury cell is only possible because the hydrogen evolution overpotential is very large at both mercury and sodium amalgam. Table 3.2 shows that reaction C(i) is thermodynamically more favourable than reaction D by 1.6 V, yet the formation of sodium amalgam occurs without significant hydrogen evolution. At the anode, in all cells, it is necessary to form chlorine with a very low oxygen content; yet, again, in Table 3.2 it can be seen that thermodynamics indicates that reaction B(i) and not A is the preferred reaction. Hence, it is necessary to seek electrode materials where the overpotential for the desired reaction is low but, in addition, the selected material must also have a high overpotential for possible competing reactions. We shall see in section 3.2 that the development in anode and cathode materials has contributed much to the changes in the chlor-alkali industry over recent years.

**Table 3.2** Equilibrium potentials for the electrode reactions occurring in chlor-alkali cells. The values are given for the pH met in such cells and are calculated assuming 25% brine, that all activity coefficients are 1 and gases are at atmospheric pressure (temperature 298 K)

Reaction	pH	$E_e/V$ vs. NHE
A $2\text{Cl}^- - 2e^- \rightleftharpoons \text{Cl}_2$	4	+1.31
B (i) $2\text{H}_2\text{O} - 4e^- \rightleftharpoons \text{O}_2 + 4\text{H}^+$	4	+0.99
(ii) $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightleftharpoons 4\text{OH}^-$	14	+0.39
C (i) $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	4	-0.24
(ii) $2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	14	-0.84
D $\text{Na}^+ + \text{Hg} + e^- \rightleftharpoons \text{NaHg}$	4	-1.85



Equation (3.5) also shows that in order to reduce energy consumption, the  $iR$  terms should be minimized. This can partly be achieved by the development of components, e.g. membranes with low resistance and electrode materials without significant resistance and designed to minimize gas bubbles in the inter-electrode gap. In addition, the energy consumption can be reduced by decreasing the interelectrode gap and this has led to the so-called 'zero gap technology'.

An understanding of the developments within the chlor-alkali industry clearly depends on being aware of the new electrode materials and separators which have been developed specifically for this industry. Hence, the section 3.2 is devoted to cell components.

The last few pages have very much stressed the importance of energy consumption in the chlor-alkali industry. This is appropriate but it is perhaps important to remind ourselves that other factors, particularly purity of the products, environmental factors and ease of management of the cell house, are probably equally important.

## 3.2 MODERN TECHNOLOGICAL DEVELOPMENTS

### 3.2.1 Electrode materials

With the exception of the cathode in a mercury cell, there is freedom to select the anode and cathode materials according to performance. The two requirements are:

1. An anode material which evolves chlorine at low overpotential while not supporting the oxidation of water to oxygen, the latter being the thermodynamically preferred reaction.
2. A cathode which evolves hydrogen at low overpotential in alkaline solution.

It should be noted, however, that the operating environments for the electrodes are not identical in the three technologies, e.g. in a diaphragm cell the anode operates in a more alkaline medium (due to diffusion of hydroxide from cathode to anode) than in membrane or mercury cells. Also, it is only in a diaphragm cell that the cathode sees significant chloride ion in solution and this can increase corrosion problems, particularly when the cell is open-circuited. These particular difficulties will be discussed in section 3.3.2.

The general concepts of electrocatalysis and the  $H_2$  evolution reactions were discussed in some detail in Chapter 1. Here, we should notice the similarity in the chlorine and hydrogen evolution reactions. Both involve the electrode reaction of an ion in solution to give a product which is dimeric and a gas. Hence, the mechanisms which should be considered will be similar, and it is to be expected that a critical property is the strength of adsorption of hydrogen or chlorine atoms on the surface of the electrode material.

Where surface intermediates are important, the apparent current density will depend on the real surface area (i.e. the roughness of the electrode surface) and

some of the catalysis observed with many materials may be due partly to a very high surface area. Other properties, particularly stability, are essential in a potential electrode material, since a chlor-alkali cell will be expected to run for months or even years without extensive renovation or replacement of components. Moreover, the availability of the electrode material in diverse forms is helpful to innovative cell design, e.g. since mercury is a liquid, the designs of cell are restricted; in contrast, titanium can be machined into many forms broadening the shapes, sizes and form of electrodes which may be used. Hence, it is helpful if either the electrode material can be machined or worked readily, or can be coated readily onto a convenient base metal such as steel, nickel or titanium.

Throughout most of the history of the chlor-alkali industry, the anode material has been graphite or some related form of carbon. The overpotential for  $\text{Cl}_2$  evolution was as high as 500 mV and the wear rate 2–3 kg of anode carbon per ton chlorine. The high rate of anode loss predetermined the design of cell and also the management of the cell house; it was essential that anodes could be replaced easily. In an attempt to improve the anode performance, precious-metal-coated anodes (e.g. Pt on Ti) were first developed and, indeed, they did reduce the anode overpotential to about 100 mV. Such anodes are, however, expensive and not entirely stable; platinum in concentrated chloride medium is lost at a rate of 0.2–0.4 g per ton of chlorine. Hence, it was the development in the early 1960s of materials which have become known as dimensionally stable anodes (DSAs)\* which has led to the change from carbon to metal anodes; DSAs are now a family of coatings which are applied to titanium and their name arises because they are inert and very stable to corrosion and their service life can be many years. In addition, they are excellent catalysts for chlorine evolution, the overpotential commonly being < 50 mV. The coatings are based on ruthenium dioxide but they may also contain valve metal, precious metal or transition metal oxides to improve performance. Generally they are prepared by spraying a mixture of chlorides in an alcohol, commonly isopropanol, and then heating in air. Many different coating compositions of DSA have been developed, e.g. for mercury cells an intermediate  $\text{TiO}_2$  layer is used to reduce damage from shorting when the Hg and anode occasionally come into contact, while special coatings to minimize the  $\text{O}_2$  content of the  $\text{Cl}_2$  are also available. In fact, the requirements for low  $\text{Cl}_2$  overpotential and high  $\text{O}_2$  overpotential are not particularly difficult to meet and, largely for reasons associated with patent rights, other companies have developed anode coatings, e.g. those based on  $\text{PdO}_2$  and the spinels,  $\text{M}_x\text{Co}_{3-x}\text{O}_4$  ( $0 < x < 1$ ,  $\text{M} = \text{Cu}, \text{Mg}, \text{Zn}$ ). The more difficult requirements concern anode lifetime in operating conditions, although the  $\text{O}_2$  content of the  $\text{Cl}$  is also important (some low percentage of  $\text{O}_2$  is always observed). It is in these areas that the materials may differ in performance and

\* DSA is a registered trademark of Diamond Shamrock Technologies S. A. but has become used by the scientific community as a term which includes a wide range of very corrosion-resistant anode coatings.



are the key targets during development programmes. All these anode coatings must be used in carefully controlled conditions since, for example, decreasing temperature or sulphate in solution can increase oxygen evolution markedly.

The almost universal replacement of carbon by metal anodes has led, by itself, to a reduction of the energy consumption by 10–15% (the cell voltage is changed by 0.45 V in  $-2.5$  to  $-5$  V). But, in addition, the chlor-alkali industry has benefited because anode replacement is no longer an important factor in the way the cell house is run and because the titanium to be coated may be fabricated in many forms. This has helped to revolutionize cell design.

The cathode in diaphragm cells was traditionally mild steel, which was very stable to corrosion but gave rise to an overpotential of 300–500 mV. It is only since the increase in energy costs following the oil crisis of 1973 that much consideration has been given to better catalysts. A number of high area nickel alloy coatings have been described but none has been totally successful in diaphragm cells. In membrane cells, the design of catalysts is easier both because of the absence of chloride in solution and the way the cathode is used (it is not coated with asbestos which must periodically be replaced). Hence, precious-metal coatings on a nickel base and high area nickel coatings are both available and overpotentials may be as low as 50 mV. Again, this represents a further 10% energy saving.

In addition to the material of the electrode, its physical structure can also be important. At electrodes where gas is evolved, the design must permit rapid bubble release, otherwise the bubbles will contribute an additional  $iR$  loss. Hence, it is common to employ expanded metal or plates with louvres (Fig. 3.1) to release gas in the desired direction. The design of such structures, however, must ensure that there is no  $iR$  drop in the electrode itself and this may require the inclusion of additional current-carrying bars (Fig. 3.1).

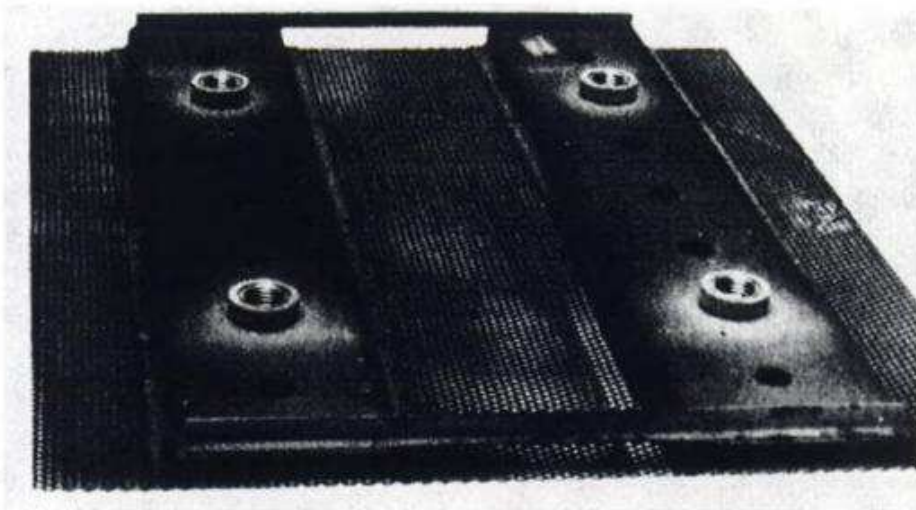
### 3.2.2 Membranes

The perfect separator in a chlor-alkali cell would:

1. pass sodium ions (but no protons) from anolyte to catholyte without the co-transport of chloride ion (leads to  $\text{Cl}^-$  contamination of the NaOH) or hydroxide ion from catholyte to anolyte (causes loss of NaOH and  $\text{O}_2$  contamination of the  $\text{Cl}_2$ ).
2. have a low resistance.
3. be stable to wet chlorine and 50% sodium hydroxide over a long period of time.

Moreover, these properties should be maintained even when the catholyte is 50% sodium hydroxide as ideally it would be when leaving the cell.

A diaphragm is porous and cannot discriminate between species. All will diffuse through its pores where there is a concentration difference. Hence, equal amounts of  $\text{Na}^+$  and  $\text{Cl}^-$  diffuse through a diaphragm from anolyte to catholyte



(a)



(b)

**Fig. 3.1** Modern anodes for chlorine cells. (a) Horizontal dimensionally stable anodes for a mercury cell. (b) Vertical dimensionally stable anode for a diaphragm cell. (Courtesy: OxyTech Systems, Inc.)

in a diaphragm cell and the caustic soda produced must therefore be contaminated heavily with chloride ion. Also, the catholyte leaving the cell cannot contain more than 10% sodium hydroxide since otherwise hydroxide-ion diffusion to the anode becomes significant and oxygen as well as chlorine is evolved. Thus, prior to sale, the sodium hydroxide produced in a diaphragm cell must be concentrated by evaporation to a 50% solution.



On the other hand, cation exchange membranes are theoretically capable of meeting all the criteria set out above. It is, however, only in the last 20 years that membranes with properties approaching those required have become available and they have been the basis for the development of membrane cell technology in general. The chemical stability is obtained by manufacturing the membranes from perfluorinated polymers while the ionic conductivity results from using monomers with side chains with terminal acid groups. The polymers have been shown to have a structure with hydrocarbon-like zones and the acid groups collect together so as to form channels through which cations can pass. The cation selectivity may arise from the size of these channels. Two basic types of membrane were developed, based on strong-acid and weak-acid functions and typical structures are shown in Fig. 3.2. Their physical and chemical properties are compared in Table 3.3. In many respects, the strong acid membranes have superior properties. The key drawback is, however, their inability to permit the production of high caustic soda concentrations ( $> 15\%$ ). This results from back-diffusion of sodium hydroxide through the membrane from catholyte to anolyte when the catholyte is very concentrated sodium hydroxide, a property arising because of the high water content of this hydrophilic polymer. In contrast, the weak acid membrane allowed the direct production of 30–40% caustic soda without significant loss of current efficiency. But these membranes have a rather high resistance, particularly if they are in contact with an acidic solution so that the carboxylate groups become protonated. Hence, it is not possible to use an acidified anolyte with the weak acid membranes and this leads to an increase in oxygen evolution (and, hence,  $O_2$  contamination of the  $Cl_2$ ) as well as reducing the lifetime of anode coatings. Clearly, with either type of polymer, the electrical

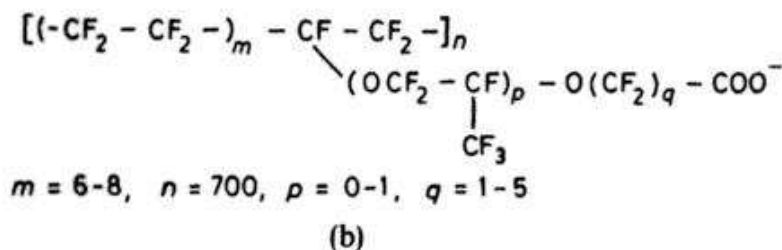
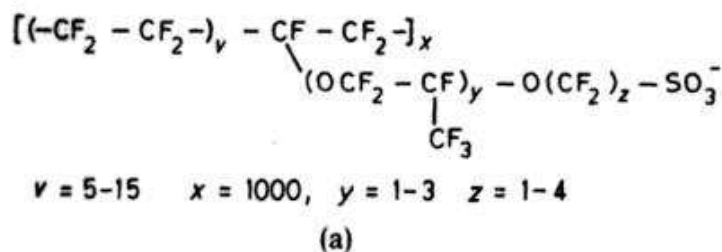
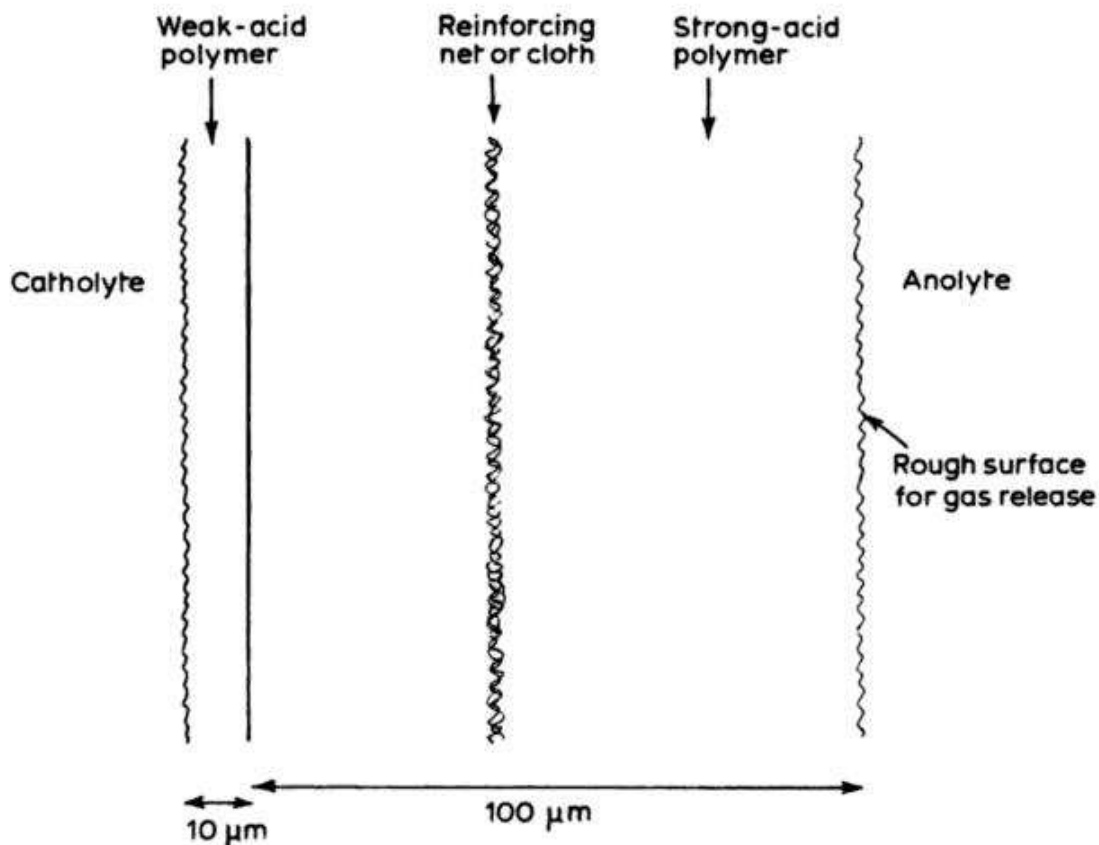


Fig. 3.2 Structures of typical perfluorinated polymers used for ion-permeable membranes in the chlor-alkali process. (a) Strong acid. (b) Weak acid membranes.

**Table 3.3** Comparison of membrane properties of importance in the chlor-alkali process

	Strong Acid Membrane	Weak Acid Membrane
Ion-exchange group	-SO <sub>3</sub> H	-COOH
pK <sub>A</sub>	< 1	3
Water content	High	Low
Current efficiency at high NaOH concentration	Low	High
Electrical conductivity	High	Low
Maximum current density	High	Low
Chemical stability	Very good	Good

**Fig. 3.3** Modern bilayer membrane for the chlor-alkali process.

resistance is minimized by manufacturing the membrane as a very thin sheet (c. 0.1 mm) and in order to impart physical strength, the membranes are reinforced with fine plastic nets.

Neither the weak- nor strong-acid membranes had all the properties desired by the industry. Hence, further development work was carried out and led to the bilayer membranes (Fig. 3.3) where a strong acid membrane is coated on the

catholyte side with a thin layer of weak-acid membrane. This combination gives a good sodium ion conductivity, only strong-acid membrane is exposed to the anolyte so that acid may be added to the anolyte, while the weak-acid layer imparts a barrier to sodium hydroxide transport from catholyte to anolyte. Several American and Japanese companies now market such bilayer membranes and they permit the production of 30–40% sodium hydroxide and low O<sub>2</sub> content Cl<sub>2</sub> with good current efficiency (section 3.3.3). The bilayer membranes are produced by several techniques including lamination, grafting and chemical conversion of some of the sulphonic acid groups to carboxylate groups. This latter technique is probably to be preferred since it allows good control of the gradient of the change in chemical composition. A further sophistication now introduced is surface roughening and/or modification to allow ready gas release from the membrane in a zero gap configuration.

As with the electrode coatings, the membranes only operate to specification under tightly controlled conditions. In particular, the brine and catholyte feeds must be highly purified. Sulphate and group II metals lead to precipitation within the membrane while heavy metals (and iron from corrosion) complex the carboxylate groups and cause an increase in membrane resistance.

### **3.2.3 Engineering and control equipment**

As in all chemical engineering, a major trend has been towards the complete utilization of all raw materials and energy and, for example, all heat from exothermic reactions or Joule heating is used elsewhere in the plant. Moreover, the plants have had to change in order to comply with the legal requirement to monitor and control emissions of possible pollutants; in the chlor-alkali industry the major concerns have been mercury and chlorine itself. Normally, both the atmosphere and the effluent will be monitored for Hg and Cl<sub>2</sub> and the hazards have been much reduced.

Although, as noted above, the fear over the transportation and storage of chlorine has led to a trend towards many smaller, on-site plants, the majority of the chlorine and sodium hydroxide is manufactured in large plants. Here, the tendency has been to build larger plants and to intensify their operation. In particular, current densities have been increased and cellrooms have become larger. This has required the design of very heavy current rectifiers and switchgear; mercury cells operate at up to 500 kA. The cellroom will thus require equipment to operate at this rating and to rectify grid a.c. to d.c. Perhaps the first step in the modern era was the introduction of silicon rectifiers which improved the conversion efficiency from 86 to 99%; they can produce d.c. current at 240 V and it is normal to arrange the cellroom so that the centre of a series of cells is earthed. Then there is a 240 V drop on either side of the earth making the total voltage drop available in the cellroom 480 V. Subsequently, the electronics revolution has had a substantial impact on the organization and control of a chlor-alkali plant. It is now possible to measure and record on a computer, data



from each cell, flow and reactor. The aim is to detect problems as they arise and to have a measure of automatic control, e.g. of anode-cathode gaps in a mercury cell.

The computer has a second and larger control function. The optimum conditions in the cellroom are time dependent, e.g. in the UK the cost of power from the national grid is less at off-peak times, when it will be economic to run the cellroom on a high load and current density. On the other hand, the load should be reduced when power is expensive, and the computer is programmed to make these changes automatically while ensuring the desired daily production rate.

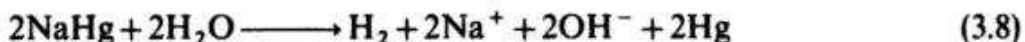
### 3.3 CHLORINE CELL TECHNOLOGIES

#### 3.3.1 Mercury cells

In a mercury cell the electrode reactions are:



and the sodium amalgam is hydrolysed:



in the presence of a catalyst in a separate reactor known as the denuder. The reversible cell potential is  $-3.16$  V and, provided the anodes are DSA, the overpotentials associated with the electrode reactions are very low. The normal cell voltage is about  $-4.50$  V and the additional voltage is required to drive the current through the Hg-DSA gap, the electrodes and the cell connections and busbars.

A typical mercury cell is shown in Fig. 3.4. It consists of a large, shallow trough, dimensions  $15 \times 2 \times 0.3$  m, with a steel base which slopes slightly from end to end so that the mercury can flow along the bottom of the cell. The coated, expanded titanium dimensionally stable anodes (DSA) (Fig. 3.1), each of approximate dimensions  $30 \times 30$  cm, enter the cell from the top and are arranged parallel to the Hg surface with an anode-cathode gap of less than 1 cm. The cell will have about 250 such anodes so that most of the mercury is covered by anode; the cell approximates to a horizontal parallel-plate configuration. The brine - concentration 25% and temperature  $60^\circ\text{C}$  - flows through the cell and leaves at 17% either to be recycled through the salt deposit or, after treatment, to be discharged. The chlorine gas leaves the cell at the top while the sodium amalgam (approximately 0.5% sodium) leaves at the base, passes through two washing weirs to remove all the sodium chloride solution and enters the denuder.

The denuder is a cylindrical reaction vessel packed with graphite balls impregnated with a transition metal (e.g. Fe or Ni) to catalyse the amalgam

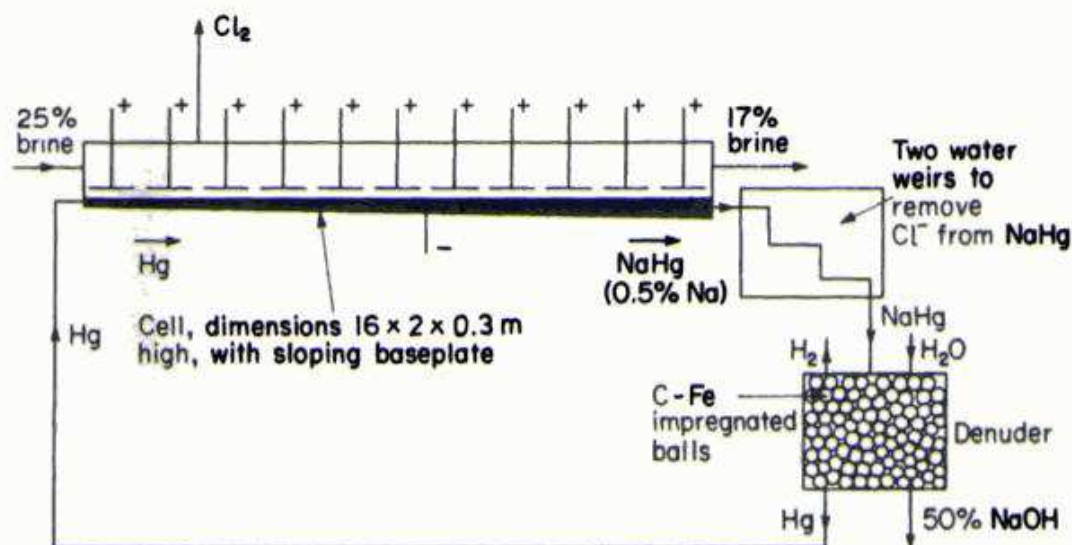


Fig. 3.4 A sketch of a mercury cell design and the coupled Hg circuit.

decomposition. The sodium amalgam and a controlled volume of pure water flow down the graphite and react. It was noted above that the sodium amalgam water reaction is kinetically hindered; on the other hand, the reaction occurs rapidly in the denuder and is highly exothermic, because the transition metal provides an alternative surface to mercury for the hydrogen evolution reaction. The reaction in the denuder thus occurs by a type of corrosion mechanism, i.e. the reactions:

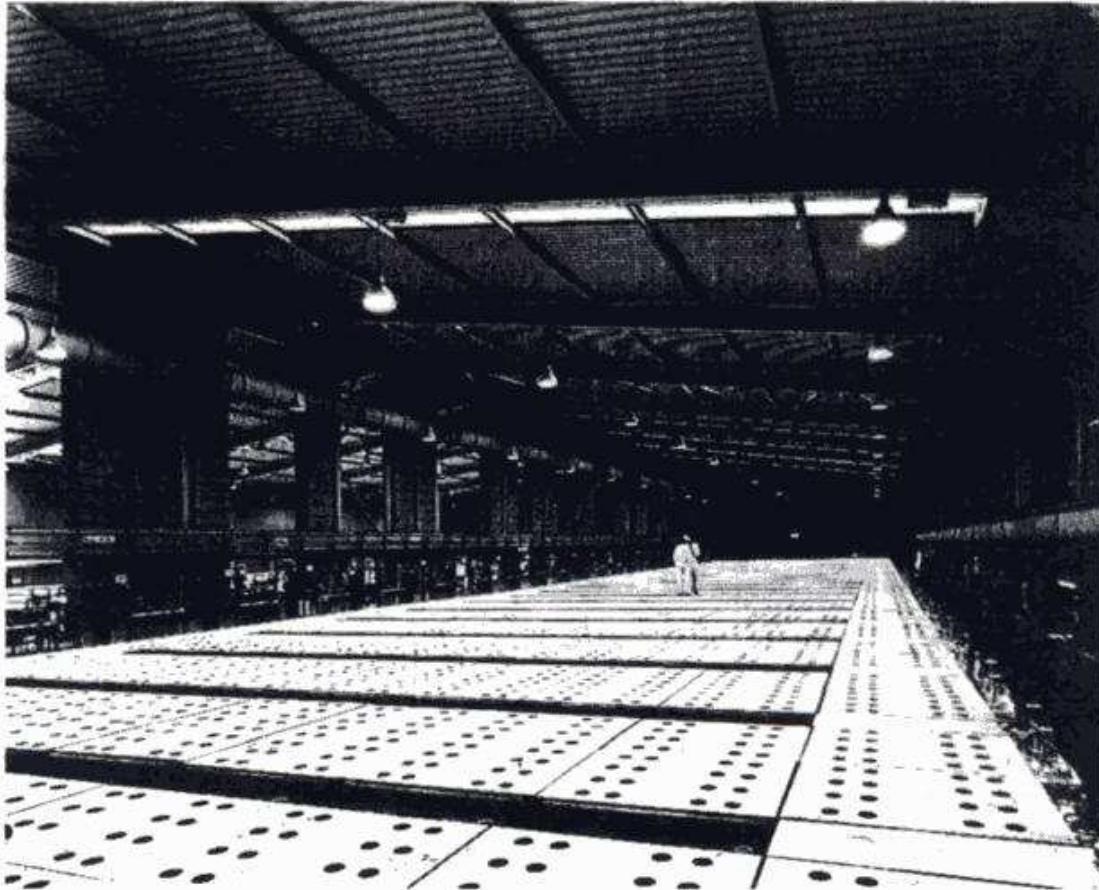


occur on different parts of the impregnated graphite surface but at equal rates so that no net current flows. The hydrogen gas leaves from the top of the denuder, and the mercury for recirculation to the cell and the aqueous sodium hydroxide separate at the bottom. Hence, by controlling the water feed rate, it is possible to produce 50% caustic soda directly.

A typical cellroom (Fig. 3.5) consists of a large number of cells in electrical series so as to make use of the available 480 V, i.e. about 100 cells. Mercury cells operate at current density in the range  $0.8\text{--}1.4 \text{ A cm}^{-2}$  so that the total cell current will vary between 180 and 315 kA and the cellroom power requirement will be 80–160 MW. It may also be noted that such a cellroom will be somewhat larger than a soccer pitch and be capable of producing about 250 000 ton of chlorine each year.

Many of the world's major chlor-alkali companies have developed their own mercury cells and the designs will differ in the way they seek to obtain the





**Fig. 3.5** A general view of a mercury cell room. The facility contains 106 cells, each of 25 m<sup>2</sup> and a current rating of 225 kA. (Courtesy: ICI Chemicals and Polymers Ltd.)

maximum electrode area and in the arrangement of the auxiliary equipment. The development of the cells during almost a century of electrolytic chlorine and caustic soda production, and the variation in the cells recently available, are described in the texts listed at the end of the chapter.

The cellroom is only part of the plant necessary for conversion of brine into chlorine and caustic soda and the complete process is shown in Fig. 3.6. Most chlor-alkali plants are sited above, or close to, a salt dome and the brine is made by pumping water through the salt deposit. The resulting solution is not, however, pure sodium chloride and, prior to electrolysis, the group II metals must be removed since they give rise to a phenomenon known as thick mercury or mercury butter, where solid amalgam is formed in the mercury leading to shorts and possible anode coating damage as well as impurities in the sodium hydroxide. The purification process is usually by precipitation of the group II metals as hydroxides by increasing the pH with sodium hydroxide although ion-exchange methods are also available. The brine is then acidified, to avoid hydrolysis of the chlorine, heated to 60° using heat from the denuder and passed to the cell.



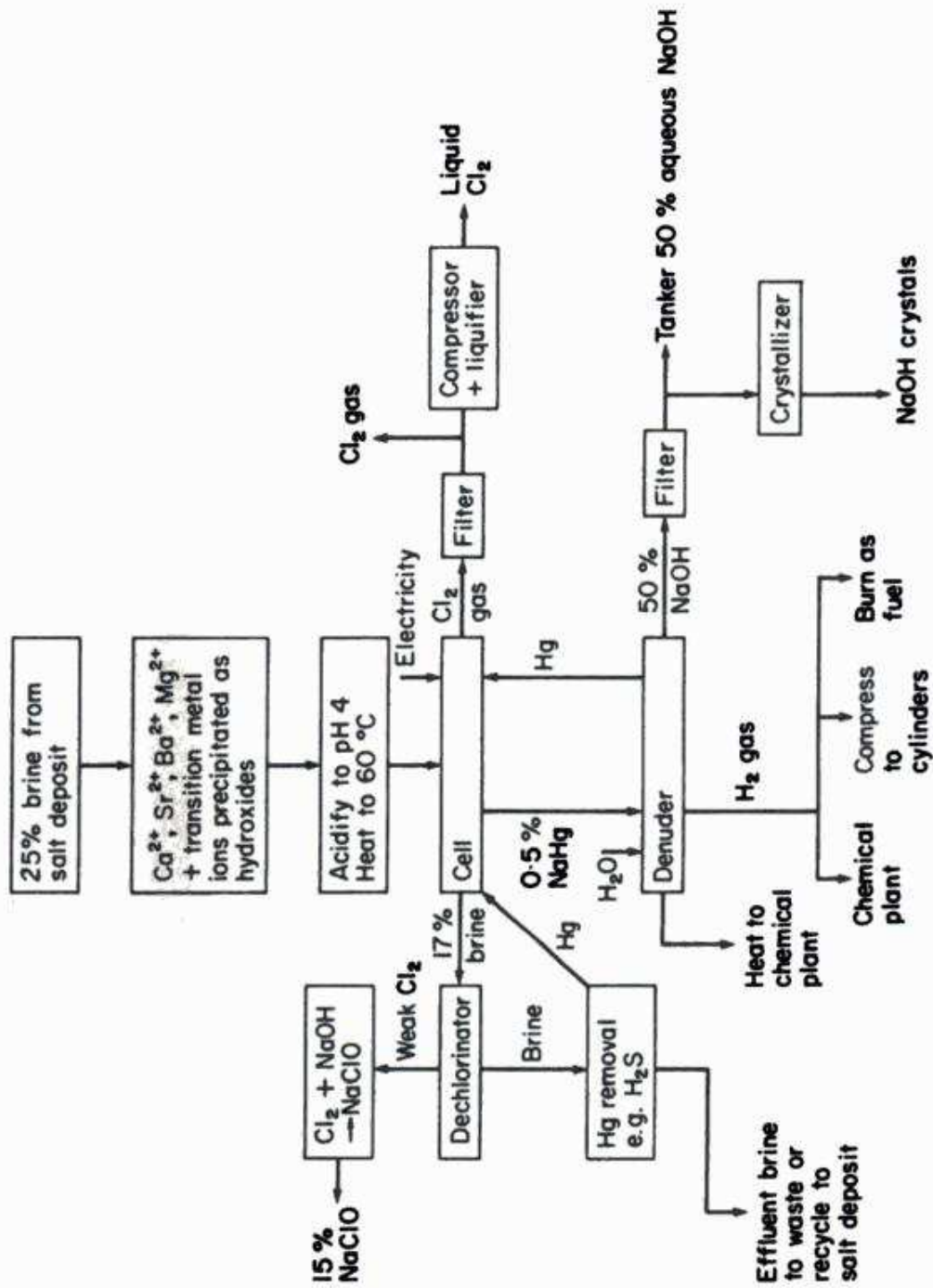


Fig. 3.6 The complete mercury cell process for the conversion of salt deposits into chlorine and 50% caustic soda.

After electrolysis and decomposition of the sodium amalgam in the denuder, all three products – chlorine, hydrogen and sodium hydroxide, must be filtered and transformed to forms required for sale. The sodium hydroxide is sold as 50% solution or pellets, and the chlorine is compressed and liquefied for storage and transport or used directly in an adjacent chemical plant. The hydrogen gas is used, if possible, as a chemical feedstock or sold as compressed gas since this gives the best financial return; otherwise, it is burnt as a fuel in the power station. The effluent brine must be treated with a stream of air to remove the residual chlorine (which is generally used to manufacture hypochlorite) and also for the removal of both finely dispersed mercury metal and mercury compounds and ions. Whether it is then recycled to the salt deposits or discharged into natural waterways will depend partly on the proximity of the boreholes and local effluent discharge practices.

### 3.3.2 Diaphragm cells

A diaphragm cell has a separator based on asbestos with various polymers added to improve its performance and the electrode reactions generate chlorine and sodium hydroxide directly (reactions A and C(ii) of Table 3.2).

The principle of a diaphragm cell is sketched in Fig. 3.7. The asbestos is deposited directly onto a steel gauze which also acts as the cathode. The anode is placed close to the diaphragm and the 30% brine is passed into the anode compartment; chlorine is formed on the anode. A fraction of the brine diffuses through the porous diaphragm and the  $H_2$  gas and sodium hydroxide are formed on the opposite side of the separator. The anodes will nowadays be a catalyst-coated titanium (e.g. DSA) and in modern cells, the steel cathode may

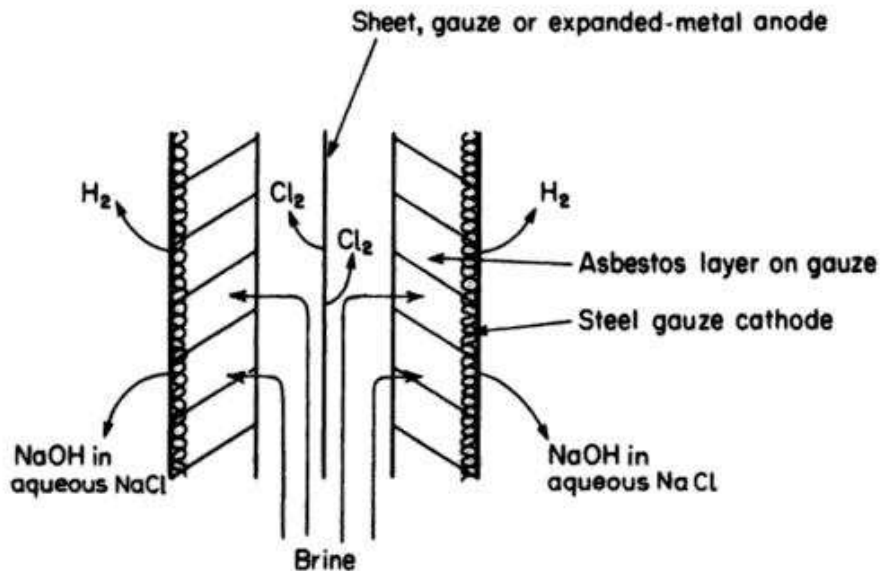


Fig. 3.7 The principle of the diaphragm cell.

also be coated with a catalyst (e.g. high-area Ni) to minimize the overpotential for H<sub>2</sub> evolution. The cathode coatings for diaphragm cells are not as good as those available for membrane cells; the difference arises because of the high chloride ion concentration at the cathode in a diaphragm cell.

The use of an asbestos diaphragm has several problems associated with it:

1. It is purely a physical barrier and all ions and other species are equally able to diffuse through it when there is a concentration gradient. As required for the cell chemistry, Na<sup>+</sup> are transported rapidly through the diaphragm from anolyte to cathode by diffusion, convection and migration. But an almost equal quantity of Cl<sup>-</sup> accompanies the Na<sup>+</sup> ions into the cathode region so that the caustic soda formed must contain a high chloride content. Moreover, the concentration of hydroxide ion formed at the cathode must be restricted to below 12%, otherwise diffusion of hydroxide ion from the cathode into the anolyte becomes significant. This leads to loss of chlorine by hydrolysis to hypochlorite and formation of oxygen at the anode and, hence, contamination of the chlorine. Low oxygen DSA were developed to minimize the latter problem.

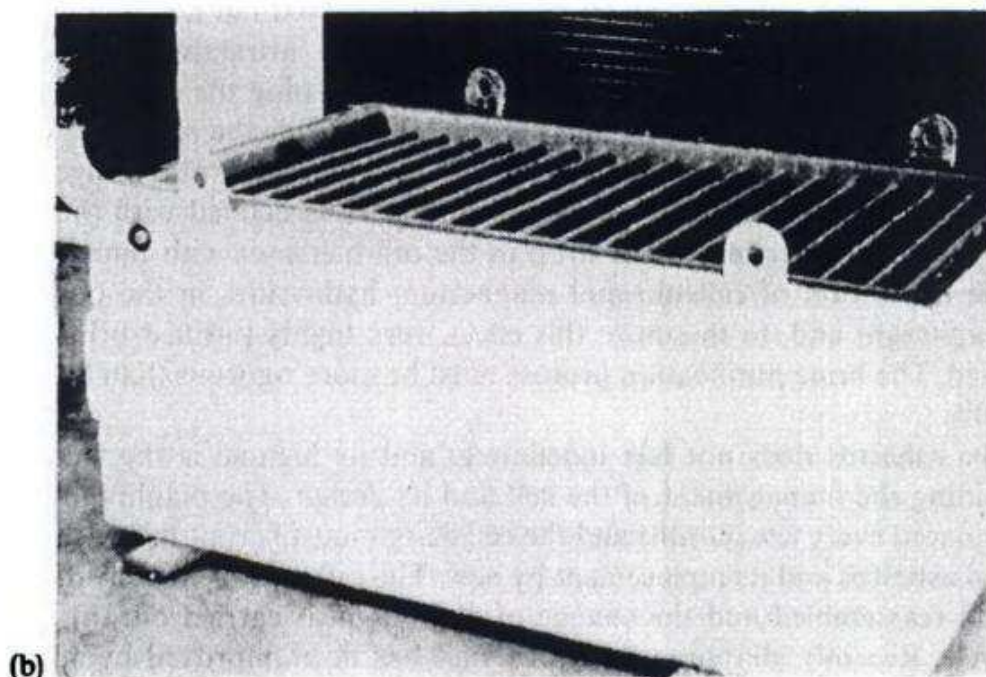
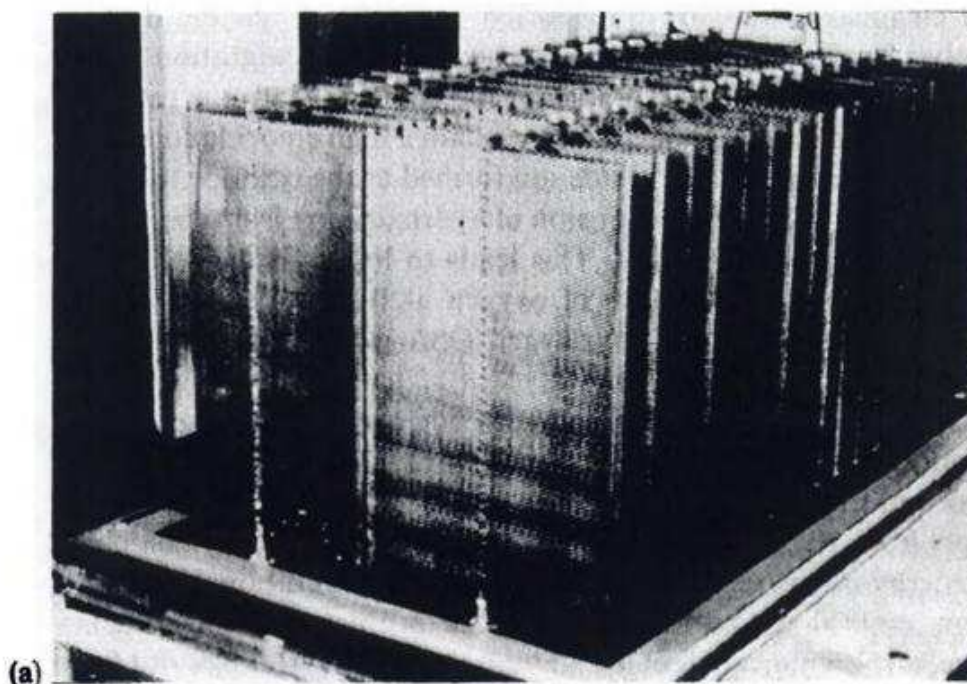
The limitation of the sodium hydroxide concentration to 12% means that an additional step must be introduced into the process if this product is to be traded in its normal form, i.e. 50% solution. The evaporation of water (note, to get from 10 to 50% solution, about 80% of the water must be removed) is an energy-intensive process which also requires additional plant. The evaporation stage does, however, reduce the problem from Cl<sup>-</sup> contamination since, on cooling, much of the sodium chloride crystallizes-out from the 50% sodium hydroxide solution. Even so, the chloride level remains about 1% and this is unacceptable in many applications, for example it increases corrosion problems in any situation where the sodium hydroxide contacts metals. Certainly, diaphragm plants are most attractive, if the sodium hydroxide can be used as a 10% solution containing the sodium chloride.

2. The *iR* drop in the diaphragm is considerable. While the reversible potential for the cell is about -2.2 V, diaphragm cells operate in the range -3.2 to -3.8 V and much of the additional voltage is associated with the asbestos separator. Moreover, the *iR* drop in the cell increases with time because of the deposition of calcium and magnesium hydroxides in the pores of the diaphragm and, to minimize this effect, very highly purified brine must be used. The brine purification process must be more rigorous than for mercury cells.
3. The asbestos does not last indefinitely and its lifetime is the factor determining the management of the cell and its design. The diaphragm must be replaced every few months and the cell design must permit the washing-off of old asbestos and its replacement by new. The cell must be readily dismantled and reassembled and the change of diaphragm is carried out on a routine cycle. Recently, diaphragm performance has been improved by addition of various polymers to the asbestos base.



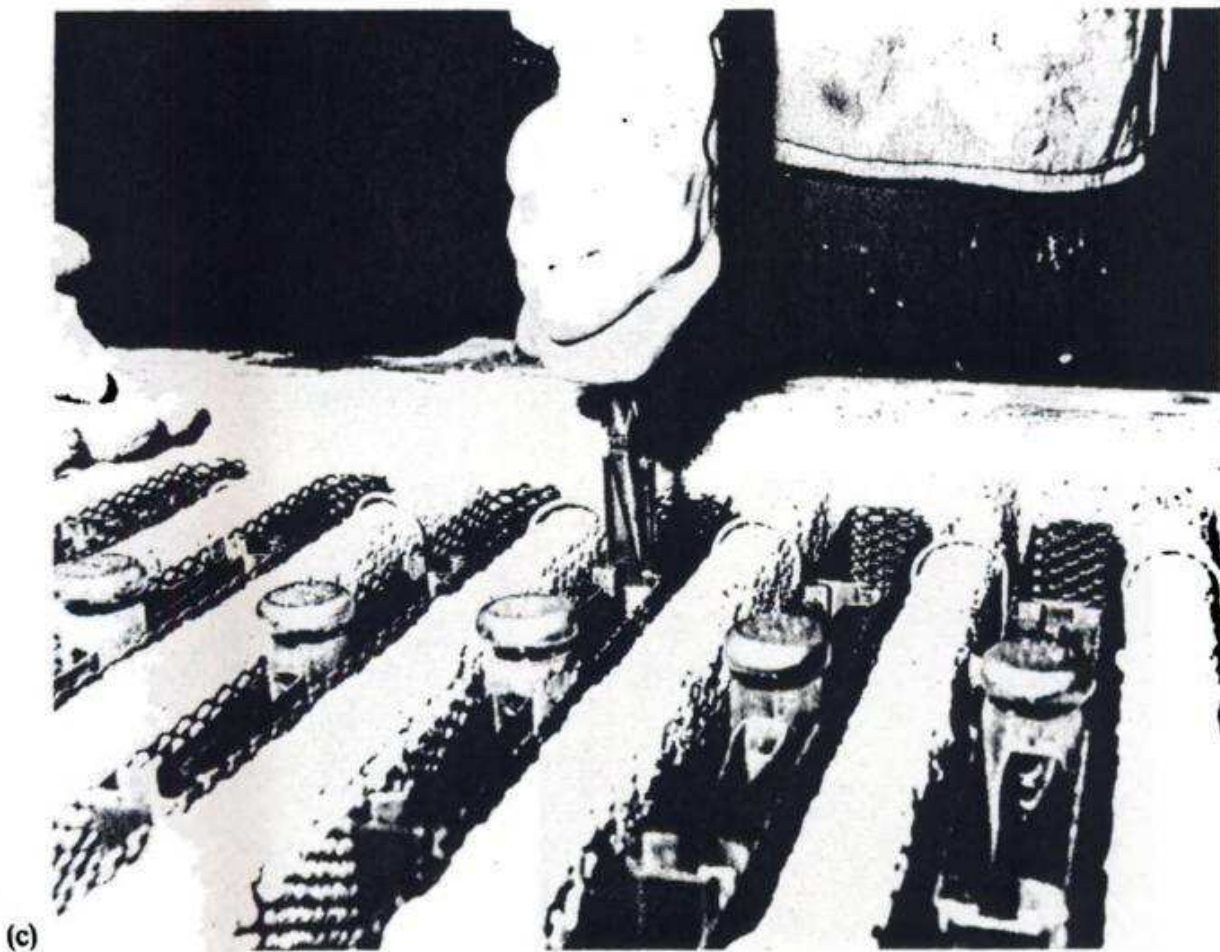
190 *The chlor-alkali industry*

Because the resistance of a diaphragm cell is high, the energy penalty of operating at high current density is economically unacceptable and the optimum current density is usually only in the range  $0.15\text{--}0.20\text{ A cm}^{-2}$ . Hence, in designing the cell, there is an overriding need to arrange for the maximum



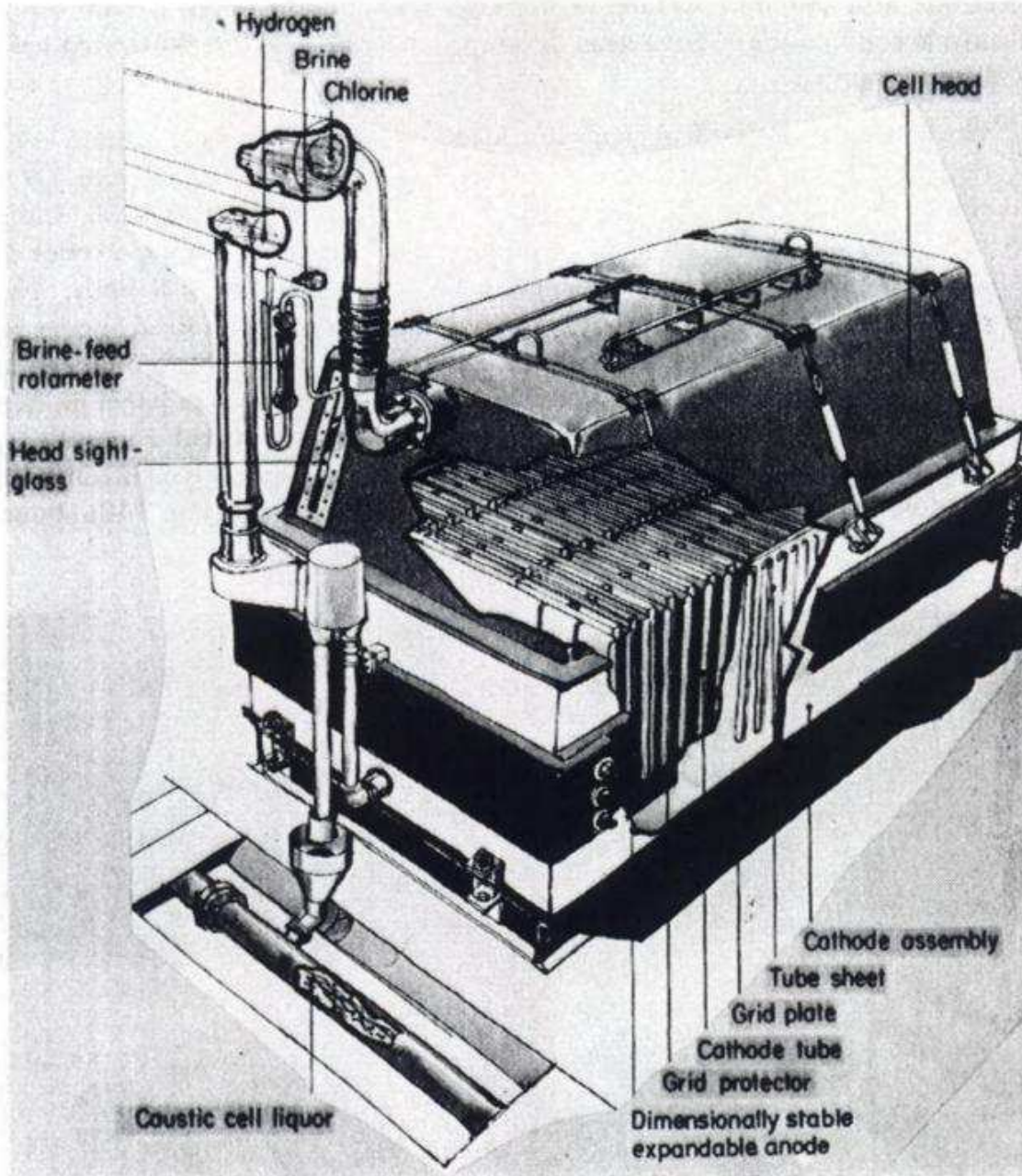
electrode area per unit volume of the cell. With this in mind, a number of electrode configurations have been developed and these will be illustrated here with two examples.

1. The first is the OxyTech Systems Inc. MDC cell, which is typical of many cells designed on the 'electric toaster' principle (Figs 3.8 and 3.9). Figure 3.8(a) shows the DSA anodes ('the toast') bolted to the base of the cell, while Fig. 3.8(b) shows the cell body containing the cathode assembly, a series of asbestos-covered steel gauze fingers extending across the cell body. The cathode assembly is dropped by crane over the cell base with fixed anodes so that each of the anodes is surrounded by cathode (Fig. 3.8(c)). The cell is sealed at the base by the weight of the cathode assembly on a polymer gasket. The cell is completed (Fig. 3.9), by attachment of electrical connections, electrolyte feeds and product take-off pipes. The cell shown has eighteen pairs of anodes and seventeen cathode fingers. The cathode tubes (Fig. 3.10), shows



**Fig. 3.8** The arrangement of a chlor-alkali diaphragm cell. (a) Anode assembly, see Fig. 3.1(b). (b) Cathode box. (c) Anode-cathode arrangement. (Courtesy: OxyTech Systems, Inc.)





**Fig. 3.9** A cutaway diagram of a complete diaphragm cell, type MDC 55. (Courtesy: OxyTech Systems, Inc.)

the view from the side, and the internal faces of the cell body are all constructed from steel mesh (possibly covered by catalyst) and the asbestos-based diaphragm is deposited onto the mesh by dipping the whole assembly into an asbestos slurry. The caustic soda and hydrogen are collected from inside the cathode assembly. The MDC 55 cell has the dimensions  $3 \times 1.6 \text{ m} \times 2 \text{ m}$  and its dry weight is almost 7 ton. It is operated in a monopolar mode



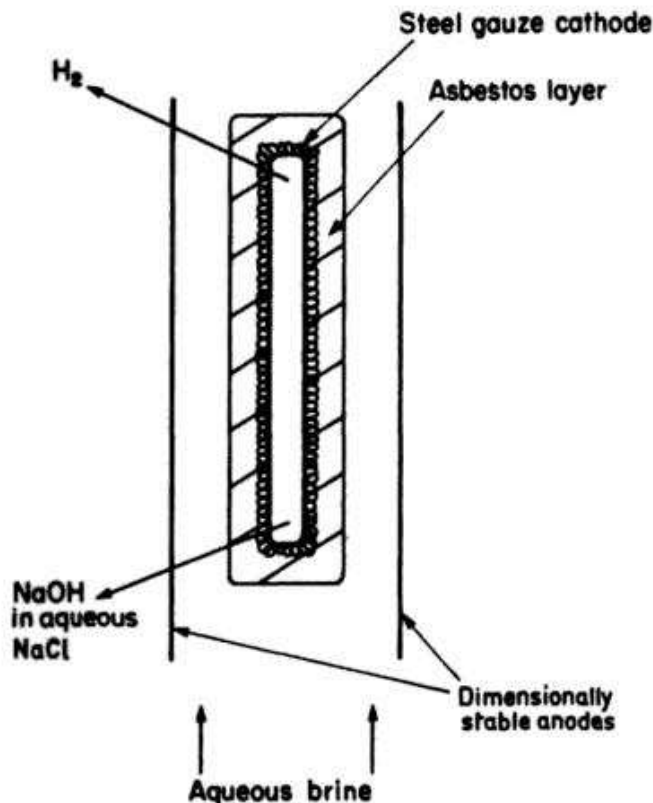
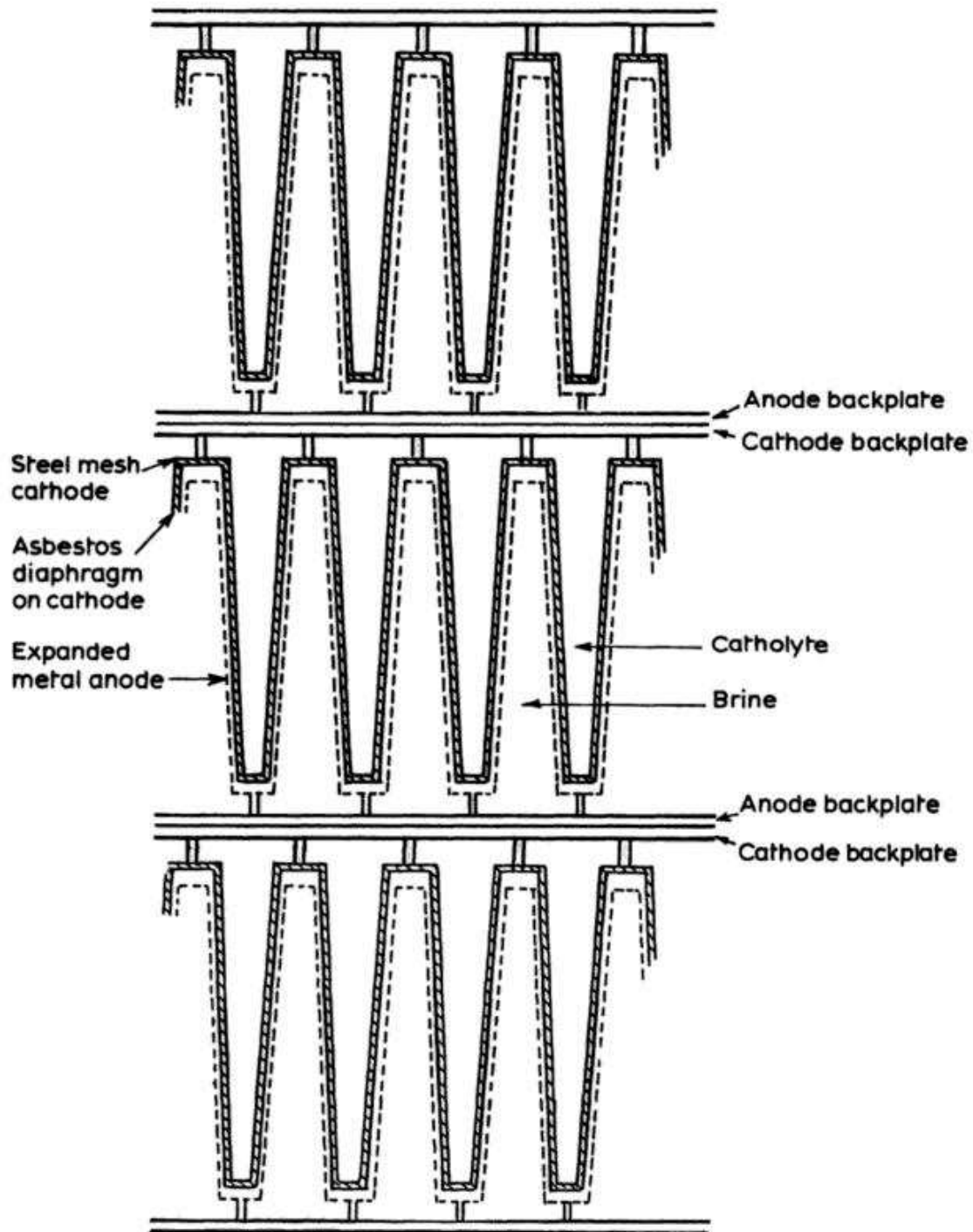


Fig. 3.10 The side view of cathode fingers in the OxyTech Systems MDC 55 cell.

and with a total cell current of 120 kA and a cell voltage of 3.4 V; it produces about 3.5 ton of  $\text{Cl}_2$  per day.

2. A quite different approach to packing a high electrode area into unit volume of cell is used in the PPG Industries electrolyser, model V-1161. The electrolyser is a bipolar unit with eleven cells. In each cell, the expanded metal anode and asbestos-covered cathode mesh are arranged as two sets of thirty interlocking fingers. The arrangement of interlocking fingers and that of cells is shown as a view from above the electrolyser in Fig. 3.11. The cell has a good space-time yield and has advantages in assembly and management. The electrolyser is made up of individual cathode and anode units which are clamped together on the rods between end elements. The design allows selection of optimum materials and is easily gasketed. Moreover, when disassembled, the asbestos is readily hosed from the cathode unit and replaced (there is better access to all points of the cathode surface than in the 'toaster' design) and in operation the diaphragm is more readily supported. The V-1161 model has an operating current of 72 kA and a voltage of 3.1 V per cell, i.e. 34 V is applied across the end plates. It produces approximately 27 ton of  $\text{Cl}_2$  per day.

The need to reduce energy consumption and to extend the lifetime of diaphragms has led to developments in the technology. These relate to improved diaphragm materials, electrode catalyst coatings and changes in cell design, e.g.



**Fig. 3.11** The view from above of a PPG V1161 electrolyser unit to show arrangement of electrodes. The sketch shows three of the  $n$  cells in the bipolar stack.

reductions in the interelectrode gap. The improvement in diaphragms results from the addition of polymers to the asbestos during formulation. These lead to lifetimes of 2–3 years as well as a lower energy consumption. This latter point is illustrated by data for the OxyTech Systems Inc. cell in Table 3.4. The improvement in diaphragm lifetime is most helpful to the process economics but

**Table 3.4** Potential distribution in recent diaphragm cells,  $I = 250 \text{ mA cm}^{-2}$

Cell type	$E^C - E^A / \text{V}$	$iR_{\text{CELL}} / \text{V}$	$iR_{\text{DIAPHRAGM}} / \text{V}$	$iR_{\text{CIRCUIT}} / \text{V}$	$E_{\text{CELL}} / \text{V}$
1. DSA box anode, steel cathode + standard asbestos diaphragm	-2.48	-0.53	-0.71	-0.27	-3.99
2. DSA expanded anode, steel cathode + polymer modified diaphragm	-2.48	-0.27	-0.46	-0.27	-3.48
3. DSA expanded anode, Ni catalyst coated cathode + polymer modified diaphragm	-2.36	-0.27	-0.46	-0.27	-3.36

Data taken from OxyTech Systems Inc leaflet, *Modified Diaphragm Cells*



it should be noted that the lifetime of catalyst coatings is estimated as 5–10 years and so it is still the diaphragm which determines cell replacement schedules.

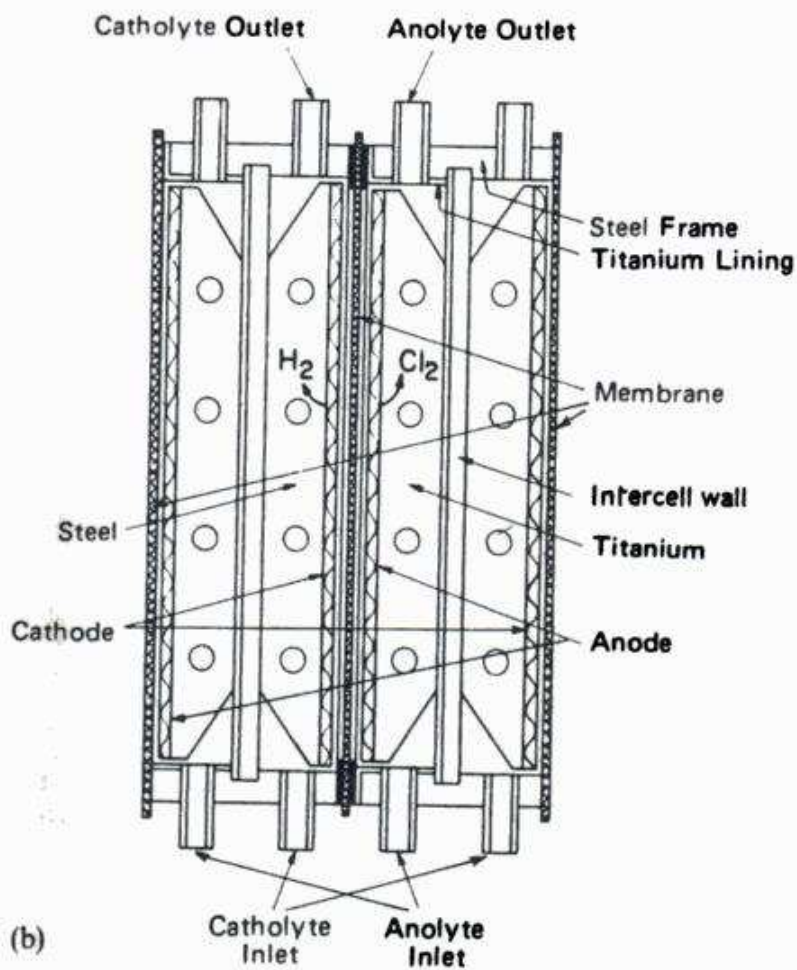
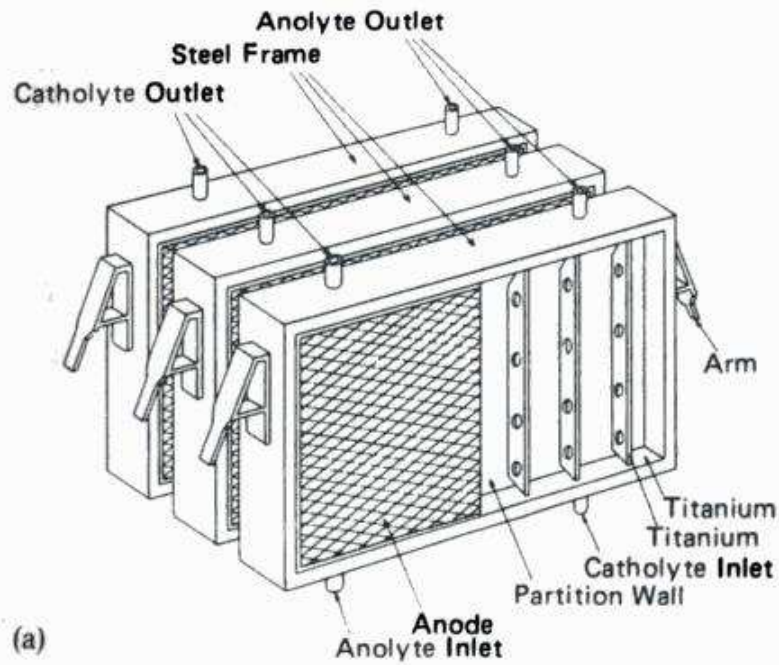
### 3.3.3 Membrane cells

The electrode reactions in a membrane cell are the same as those in a diaphragm cell but the separator is now a cation-permeable membrane. The development of modern membrane cell technology dates only from about 1970 when it was recognized that the perfluorinated membranes (section 3.2.2) had the properties essential to the chemistry of a chlor-alkali cell.

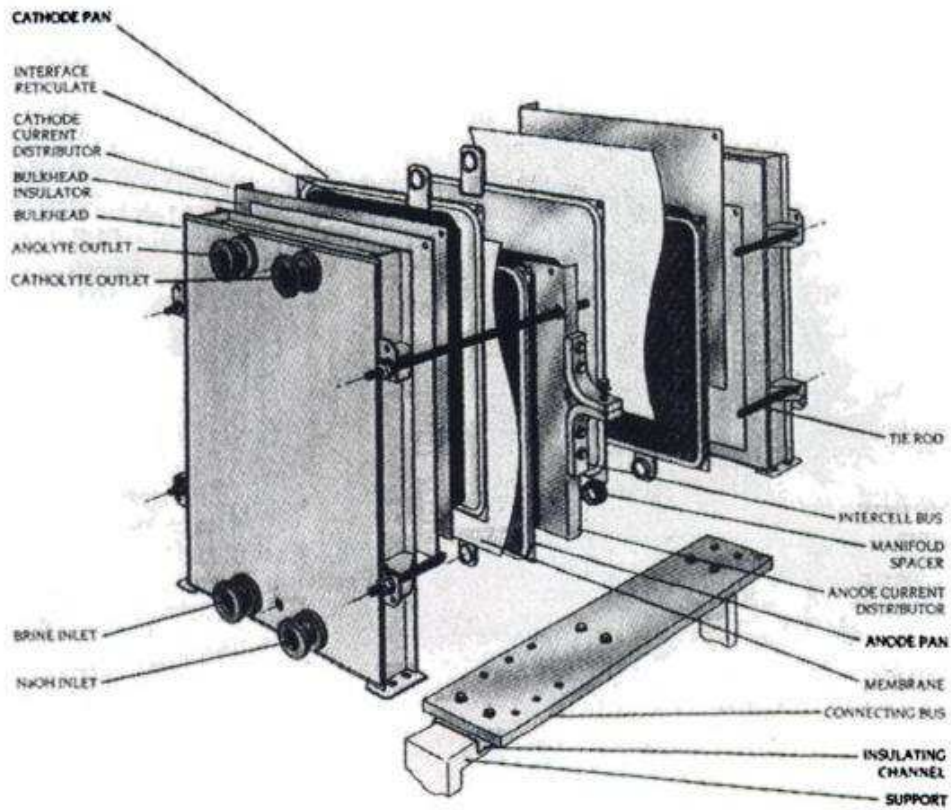
Because of the ability of the membrane to discriminate between cations and anions and to a lesser extent between sodium ions and protons, the cell is, in principle, able directly to produce 50% sodium hydroxide free of chloride ion. In fact, the membranes presently available do not quite have the necessary resistance to hydroxide ion transport and this limits the sodium hydroxide concentration which may be produced directly to below 40%; hence, an evaporation step is still necessary. The energy consumed in evaporation to produce a 50% NaOH solution is, however, much less than in the case of a diaphragm cell. For example, the concentration of 35% to 50% sodium hydroxide requires in the order of 12% the energy needed to concentrate a 10% solution. Moreover, since the membrane is designed not to permit the transport of either chloride or hydroxide ion, the chloride contamination of the sodium hydroxide is low and the oxygen content of the chlorine should be reduced compared to a diaphragm cell. The cell can be operated at a higher current density and the optimum is in the range  $0.25\text{--}0.40\text{ A cm}^{-2}$ .

The development of membrane cell technology has coincided with the rapid increase in energy costs and, therefore, in the relative importance of energy consumption. Fortunately, good catalysts are available for both electrode reactions (see section 3.2.1). Since the resistance of the membrane is also low, the search for further energy savings has been concentrated on minimizing the interelectrode gap. This has led to the so-called 'zero gap' cells where the two electrodes are in contact with the opposite sides of the membrane. This mode of operation requires further modification of the membrane surface, often by a porous inorganic coating, to ensure gas bubble release from the membrane.

More than a dozen companies throughout the world offer membrane cell technology and only two types of cell will be used to illustrate here the important features of the designs. Most membrane cells are based on a filterpress containing a series of plate and frame cells. Both monopolar and bipolar electrical connection is used. The basic structure of this type of cell is illustrated in Fig. 3.12 (note that the relative dimensions are not correct – membrane areas may be up to  $2 \times 2\text{ m}$ , although more normally  $1 \times 1\text{ m}$ , while the thickness of the electrolyte chambers is usually much less than 1 cm). The electrodes are vertical and constructed with louvres or from expanded metal so that the gases formed at the electrodes are directed to the back of the electrodes and do not stay in the



**Fig. 3.12** The construction of the Asahi membrane cell. The complete cell is made by repeating this unit. (Courtesy: Asahi Chemical Co.)

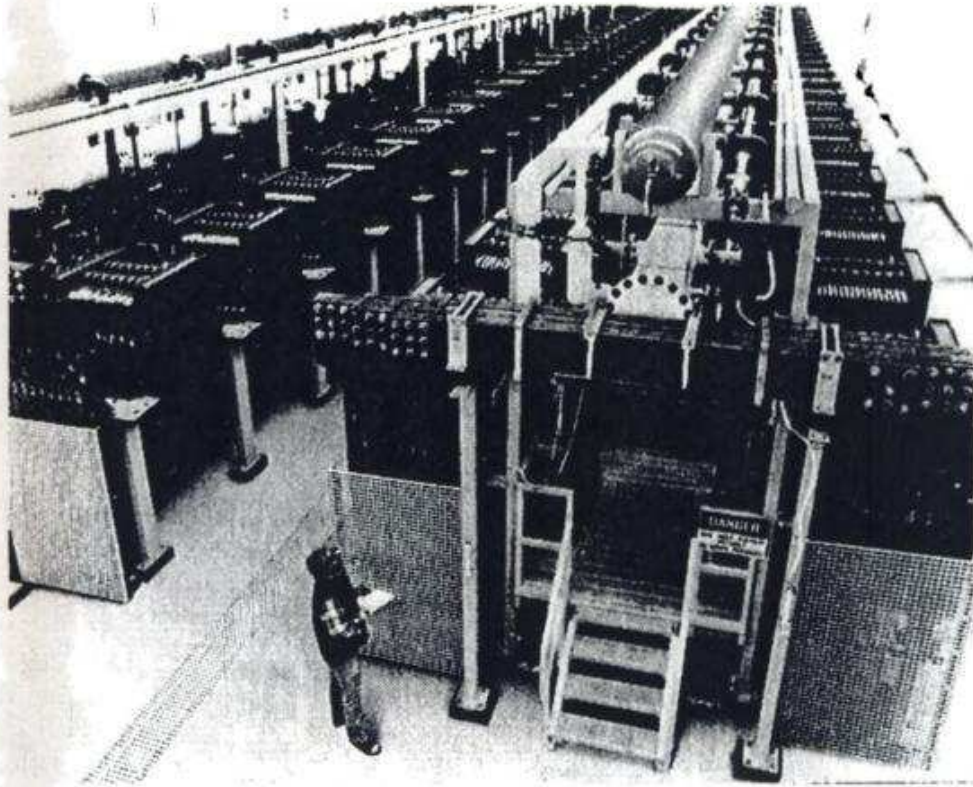


**Fig. 3.13** The components and construction of the MGC electrolyser. (Courtesy: Oxy-Tech Systems, Inc.)



**Fig. 3.14** The construction of an MGC electrolyser. (Courtesy: OxyTech Systems Inc.)



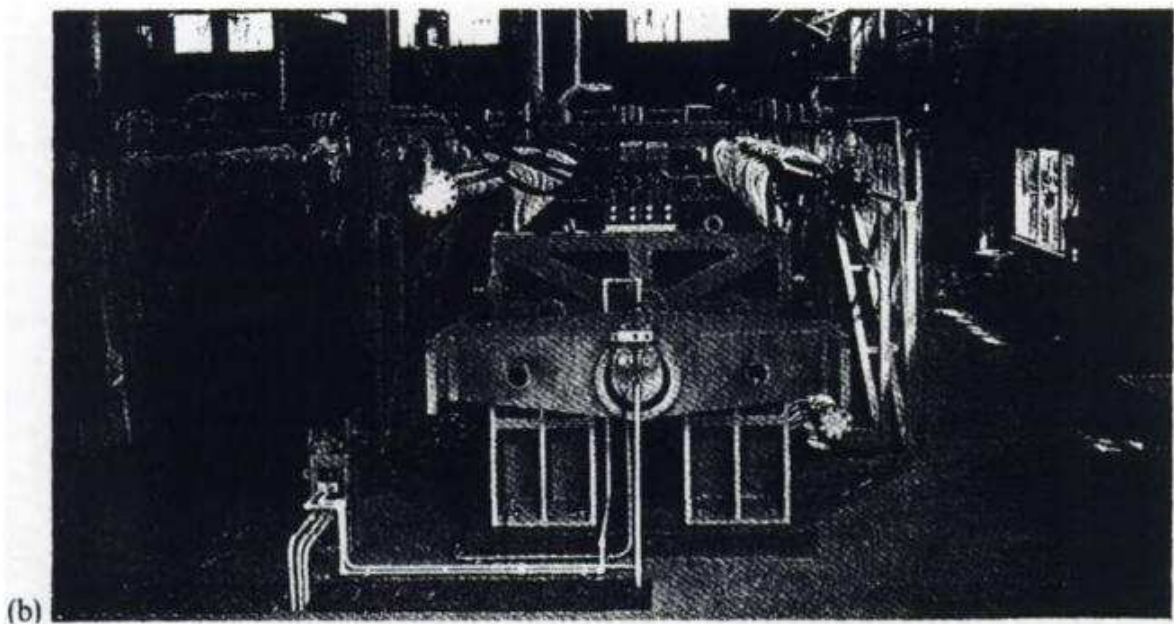
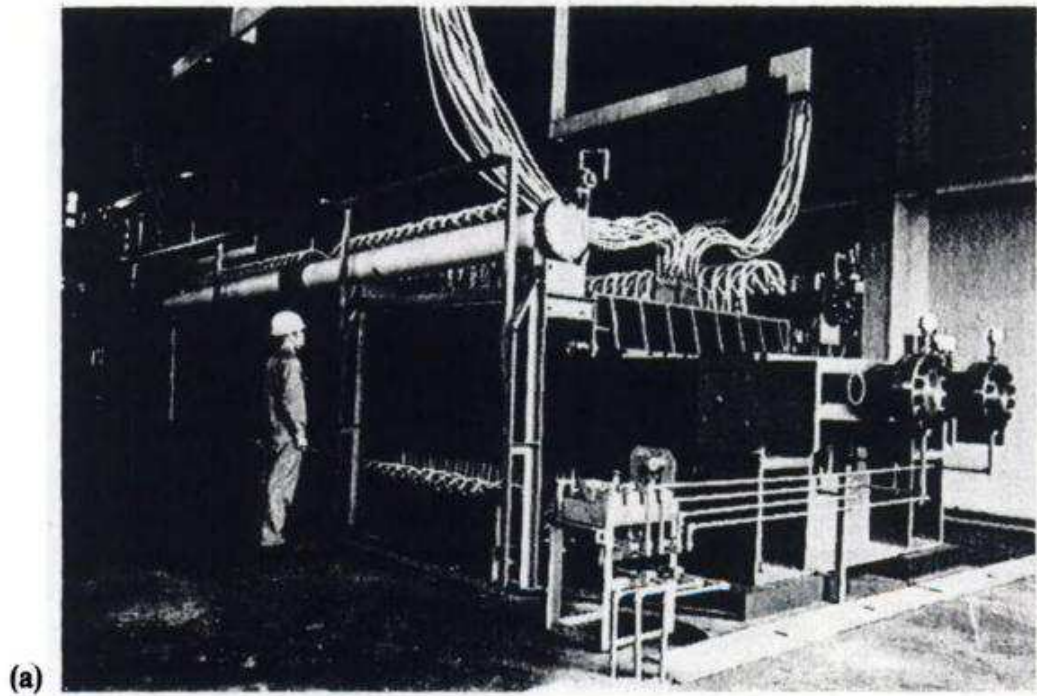


**Fig. 3.15** A membrane cell house in the USA using the MGC electrolyser. (Courtesy: OxyTech Systems Inc.)

interelectrode gap where they would increase cell resistance. The anode and cathode compartments are fed with 25% brine and dilute sodium hydroxide respectively, and the main electrolyte flow is behind the electrodes; hence, the electrolysis largely occurs at the three-way interface between membrane, electrode and electrolyte. Figures 3.13 and 3.14 show the different constructions of this type of cell, while Figs 3.15 and 3.16 show complete cell units.

ICI in England have developed a different approach to zero-gap membrane cell technology where the gasketing essentially also fulfils the role of cell body. Figure 3.17 shows the components to each cell and the way the cell units are put together in an electrolyser. The key components are the electrodes made by pressing sheet metal into a structure with two sets of 'fingers'. The gasket then fits around this electrode structure, to give a good seal and the membrane lies flat on the electrode and gasket. The electrode and gasketing are shown in more detail in Fig. 3.18 and the complete cell unit is shown in Fig. 3.19. The cell must be operated with monopolar connections and is short but wide (area  $0.21 \text{ m}^2$ ) in order to minimize  $iR$  drops in the electrode structures.

A complete filterpress stack of membrane cells will contain typically 50–100 cells and will be capable of producing up to 10 000 tons of chlorine per year. It can also be seen that it is straightforward to vary the number of cells in



**Fig. 3.16** A filterpress membrane cell facility in Japan. (Courtesy: Asahi Chemical Co.)



each electrolyser unit and, hence, to build plants with various capacities. Indeed, the present membrane cell technology has been adopted most readily for plants of about  $10^4$  tons per year and a number of such plants are operational at papermills in remote locations; there is no waste, as both  $\text{Cl}_2$  and  $\text{NaOH}$  are used in paper manufacture, and the  $\text{H}_2$  may be used as a fuel. On the other hand, very large chlor-alkali plants using membrane technology have been constructed and are operational, e.g. a 270 000 ton per year plant in Holland.

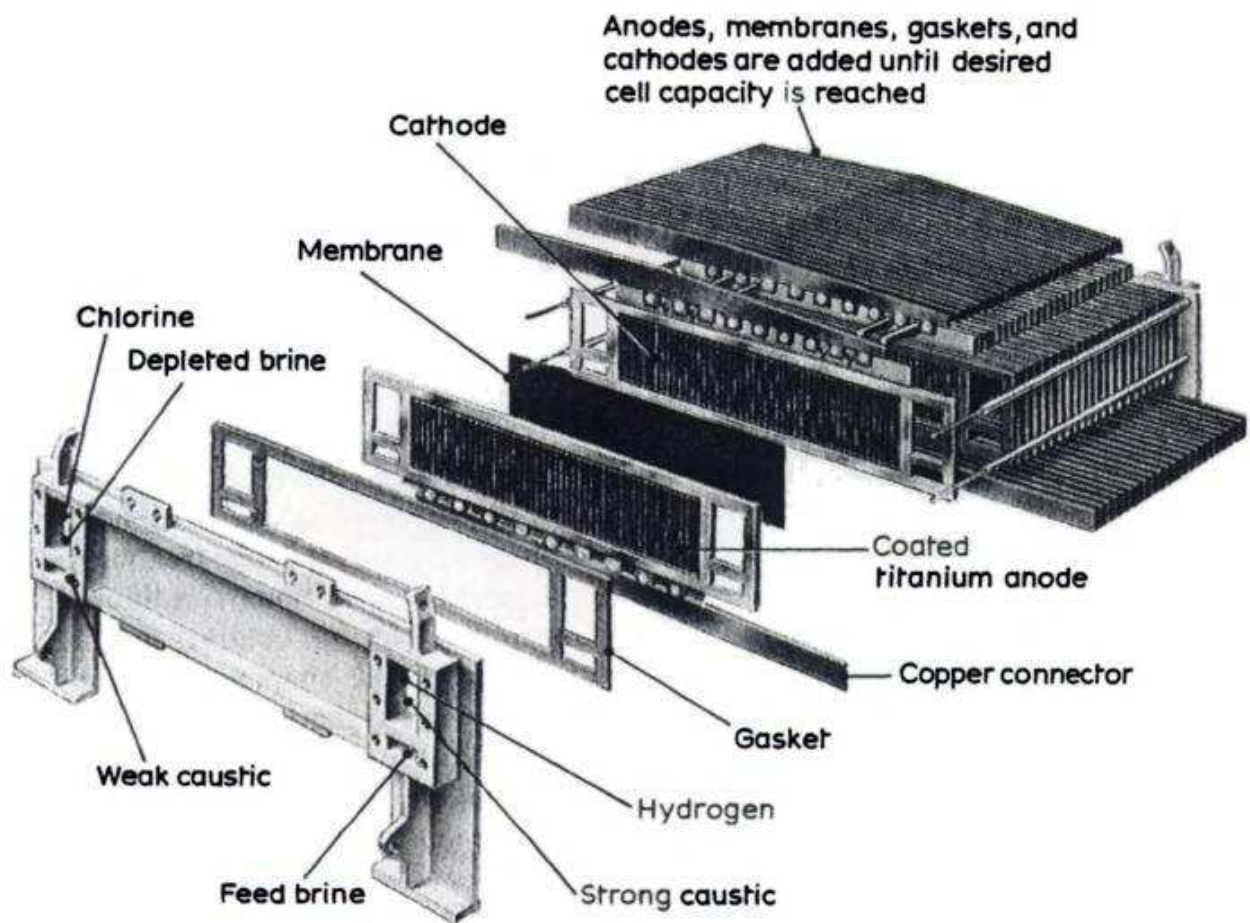
The cell voltage can be as low as  $-2.7$  V in membrane cells with coated cathodes and anodes, giving an energy consumption of only  $2200$  kWh  $\text{ton}^{-1}$   $\text{NaOH}$ . Such performance does, however, require operation under carefully controlled conditions. The temperature commonly is as high as  $90^\circ\text{C}$  and certainly the brine must be of a very high purity to avoid problems at both anode and membrane; hence, it is normal to include an ion exchange treatment in addition to precipitation of impurities. Under optimal operational conditions, membrane lifetime is now more than 3 years and the electrode coatings have a much longer lifetime. As noted at the beginning of the chapter, a further substantial energy saving is potentially possible using oxygen reduction as the cathode reaction. It is only in a membrane cell that the technology would be conceivable but even then the current view is that the additional complexity resulting from the porous cathode in a cell would not be justified.

### 3.3.4 A comparison of cell technologies

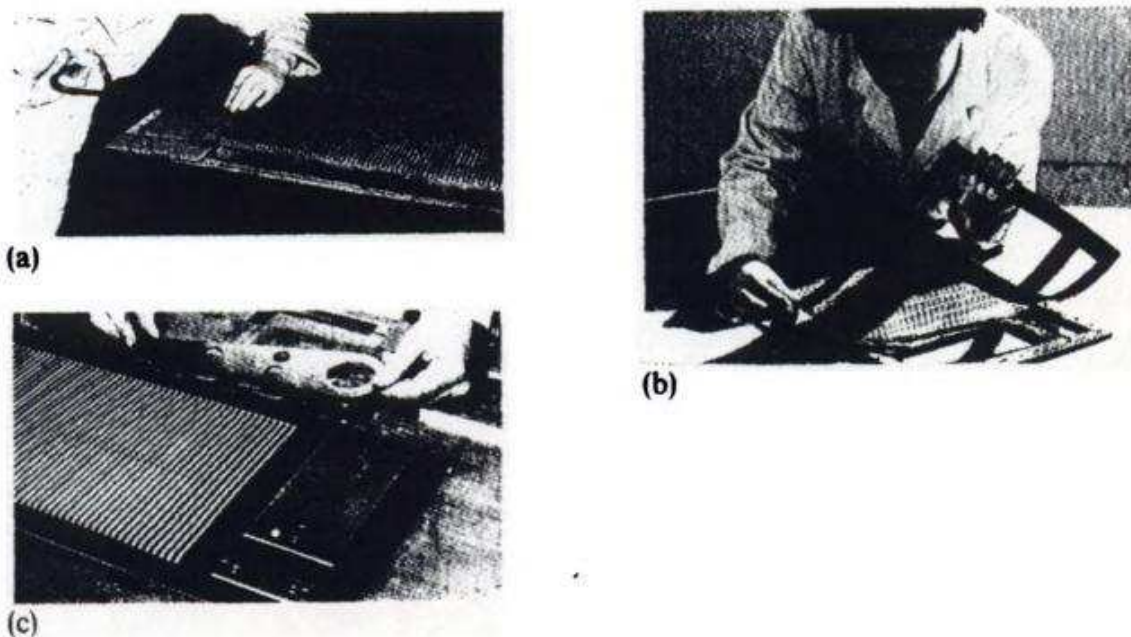
A comparison of the relative merits of the three electrolytic routes for the production of chlorine and caustic soda must be based on economics, although there are social and policy factors which must also be taken into account. It is the intention here to discuss the factors determining the economics of the processes only in qualitative terms because the uncertainties in a more exact calculation are too great. It might be noted, however, that recent published calculations would indicate that the costs of chlorine and caustic soda produced by the processes are very similar and this must be the case since mercury, diaphragm and membrane cells are all presently operated and, until recently, were all considered when new plant was to be purchased. The improvements in the membrane cell discussed above have, however, led to a situation where it is expected that membrane cells will be the preferred technology of the future. It is only lack of operational experience which, in most situations, prevents their automatic adoption when new plant is required. Certainly, the percentage of world chlorine produced in membrane cells is rising rapidly.

Typical data for the three cell technologies is summarized in Table 3.5.

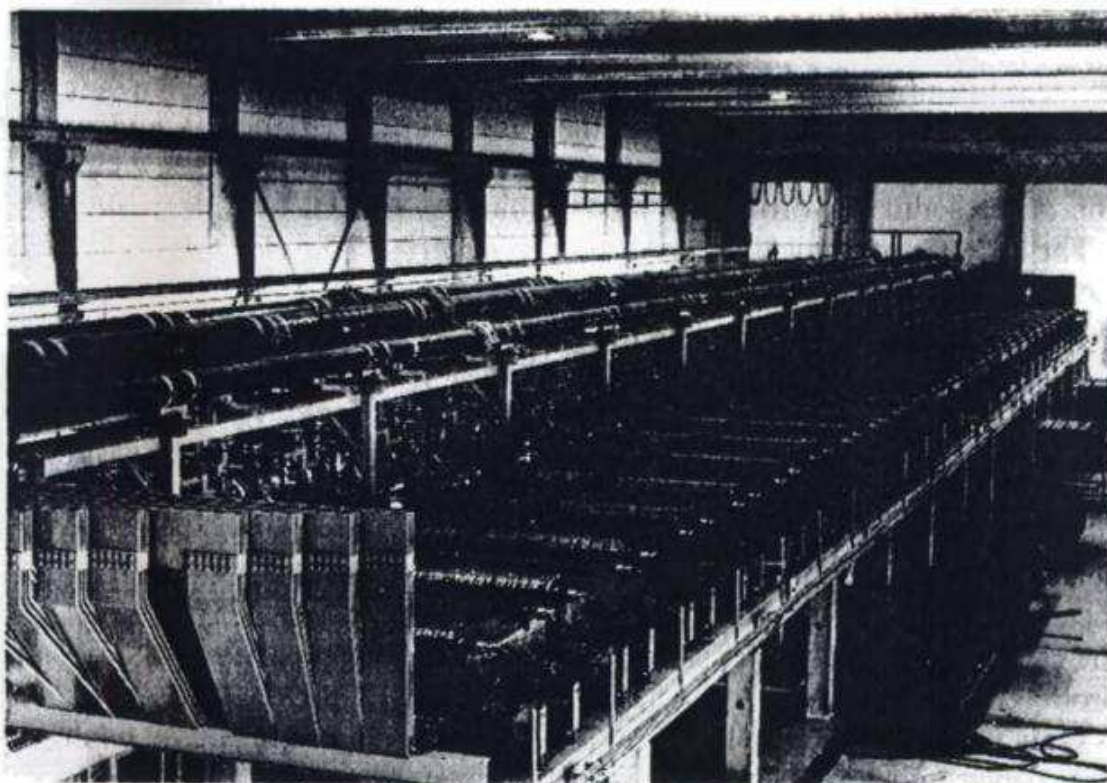




**Fig. 3.17** The design concept for the FM series of ICI electrolyzers. The module shown is the original FM21 HP electrolyser (the present SP series is shown in Figure 2.32). (Courtesy: ICI Chemicals and Polymers Ltd.)



**Fig. 3.18** Construction of the FM series of electrolyzers. (a) spacer being inserted between the blades of the electrode. (b) fitting gasket to the electrode panel. (c) complete electrode unit. (Courtesy: ICI Chemicals and Polymers Ltd.)



**Fig. 3.19** Chlor-alkali cell room based on FM21 SP electrolyzers. (Courtesy: ICI Chemicals and Polymers Ltd.)

**Table 3.5** Typical data for recent commercial chlor-alkali cells

	Mercury cell	Diaphragm cell	Membrane cell
Cell voltage/V	-4.4	-3.45	-2.95
Current density/A cm <sup>-2</sup>	1.0	0.2	0.4
Current efficiency for Cl <sub>2</sub> /%	97	96	98.5
Energy consumption/kWh per ton of NaOH			
(a) Electrolysis only	3150	2550	2400
(b) Electrolysis + evaporation to 50% NaOH	3150	3260	2520
Purity Cl <sub>2</sub> /%	99.2	98	99.3
Purity H <sub>2</sub> /%	99.9	99.9	99.9
O <sub>2</sub> in Cl <sub>2</sub> /%	0.1	1-2	0.3
Cl <sup>-</sup> in 50% NaOH/%	0.003	1-1.2	0.005
Sodium hydroxide concentration prior to evaporation/%	50	12	35
Mercury pollution considerations	Yes	No	No
Requirement for brine purification	Some	More stringent	Very extensive
Production rate per single cell/tons NaOH per year	5000	1000	100
Land area for plant, of 10 <sup>5</sup> tons NaOH per year/m <sup>2</sup>	3000	5300	2700



*(a) The initial cost of the plant*

This will include the purchase of the cells, control equipment and all the ancillary equipment for purifying the brine, liquefaction of the gases, concentration of the sodium hydroxide to a 50% solution, effluent treatment, etc.

The cells are constructed from expensive materials. The electrolyte chambers are commonly titanium in order to avoid corrosion problems, while both membranes and electrode coatings are costly components. It is, hence, desirable to minimize the number of cells and to seek operating conditions for extending the cell lifetime. In electrochemical processes, it is the current density which determines the size and number of cells necessary for the required annual production and, hence, is a key factor determining the cost of the cellrooms. It has been recorded in the preceding sections and is noted in Table 3.5 that the normal working current density for a mercury cell is very much higher than for a membrane or diaphragm cell, and the effect of this parameter combined with the easier scale-up of such cells may be seen in the comparison of the annual production rates.

Only with a mercury cell can 50% NaOH be produced directly. Diaphragm cells, since only producing 12% NaOH, must be combined with extensive evaporation plant; membrane cells require considerably less. Mercury cells also require the least stringent brine purification since they can tolerate relatively high concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Membrane cells require very highly purified brine and, hence, more plant, e.g. ion exchange columns as well as alkaline precipitation. On the other hand, in order to meet legal requirements, mercury cell facilities must have plant to treat the effluent for the removal of mercury, and the presence of large quantities of mercury increases monitoring requirements in the plant. Finally, the cost of the mercury and pumping it are not negligible!

*(b) Operating costs*

Operating costs include labour, replacing components and the rent and taxes on the land. A comparison of the latter is very unfavourable to diaphragm cells where almost twice as much land is necessary because of the low current density and the need for evaporation plant. Membrane and mercury cells have similar land requirements because the former are packed together closely in a filterpress and to some extent the electrodes scale vertically. All the processes are largely automated and, hence, the difference in labour costs is likely to arise because of a variable incidence of component and pipework failure. The need to replace diaphragms on a routine cycle certainly increases the labour costs for the diaphragm cell process; improved diaphragms may operate for 2–3 years. The lifetime of membranes is very sensitive to operating conditions but operation for upwards of 3 years can be achieved. Electrode coatings, in general, have much longer lifetimes. The replacement of membranes is now an easier operation than replacement of diaphragms.

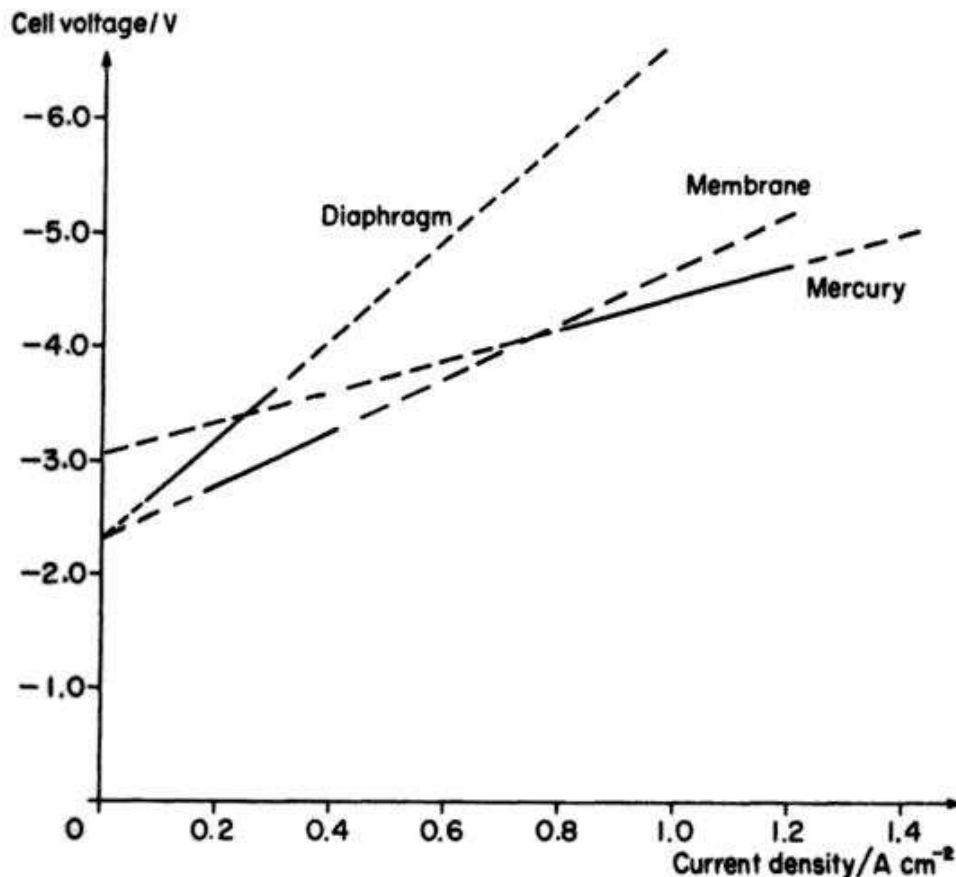


*(c) Value-added during the process*

The value-added depends on both the cost of the raw materials and the value of the products. The raw materials for all three processes are similar but differences in the purity of the products will affect the price which may be obtained for them. The diaphragm cell process again comes a poor third since the sodium hydroxide is high in chloride ion and the chlorine contains a higher content of oxygen. Hence, the diaphragm cell becomes much more favourable if the sodium hydroxide is not to be sold on the open market and the internal use can tolerate the chloride ion impurity. The most favourable situation is when the sodium hydroxide may be used as a 10% solution, direct from the cell, thus avoiding the need for concentration. This is often possible when the sodium hydroxide is used to neutralize acid during organic synthesis.

*(d) The cost of energy*

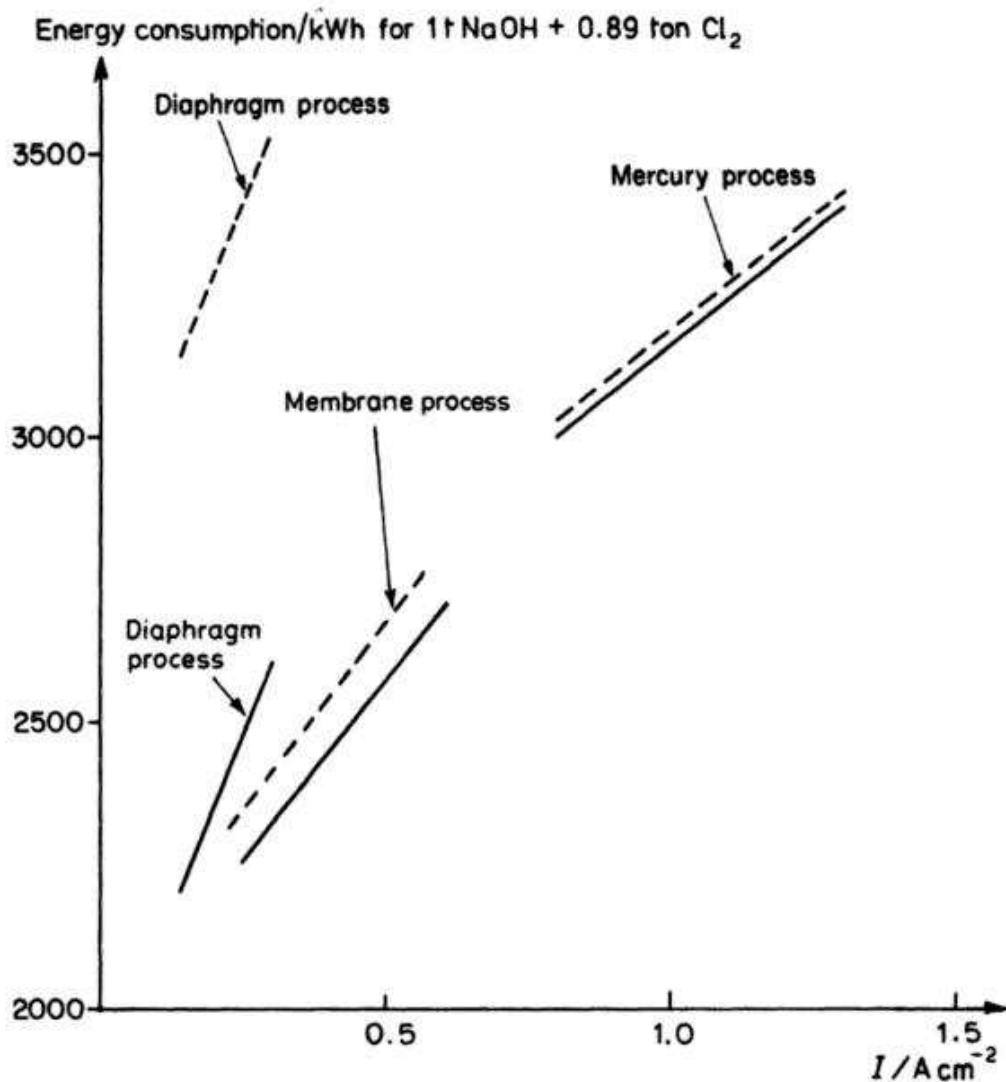
Figure 3.20 shows current density-cell voltage plots for cells of all three technologies, the full lines indicating the normal operating regions. The plots are all linear and this indicates the total predominance of the  $iR_{\text{CELL}}$  term in equation (3.5). The cell voltage is, however, only important in so far as it



**Fig. 3.20** Cell voltage versus current-density plots for the three types of chlor-alkali cell. The full lines indicate the normal operating regions.

determines the energy consumption of the cell and Fig. 3.21 therefore shows the relationship between energy consumption and current density; both the energy consumed in the electrolysis and the total energy to form chlorine and 50% aqueous sodium hydroxide are included, the latter being the normal basis for comparison.

In seeking the conditions for operating the cell, both the absolute energy consumption and the slope of the lines (essentially the cell resistance), are important since there will be a trade-off between energy consumption and the rate of production (i.e. current density) when the total cost is considered; the slopes indicate the additional energy which must be consumed to permit a faster production rate. It is the low resistance of the mercury cell which allows the use of high current densities without an unreasonable voltage penalty.



**Fig. 3.21** A comparison of the energy consumption in the three cell technologies for chlor-alkali production. The full lines represent electrolysis only; the broken lines, total energy consumption, including evaporation and heating the electrolyte.

It will be seen that the energy consumptions of the three cells are not dissimilar before concentration of the NaOH. Until now it has been considered worthwhile to increase current density (i.e. production rate) rather than conserve energy as cell technology has been improved. This decision is changing as electric power becomes more expensive and it is conceivable that current densities might even be reduced to decrease the energy requirement. Moreover, the improvement in the energy consumption of membrane cells is a key factor in their increasing share of the market. The necessity for evaporation and, hence, the market for the NaOH, has a large influence on any decision to install a diaphragm plant.

*(e) The choice*

The choice of cell technologies has not been made on the basis of an economic assessment alone. It is clear from the above that the mercury cell, despite being the oldest of the technologies, has many substantial advantages. It has, however, come under strong pressure because of the fear of mercury pollution. The dangers of the industrial use of mercury became fully recognized following several deaths due to mercury poisoning at Minimata in Japan in the 1950s. Two responses to the problem of potential mercury poisoning are possible: (1) to control carefully the use of mercury in the plant and ensure that effluent does not contain harmful amounts of mercury, or (2) to discontinue completely using mercury. The USA has decided to replace mercury cells as rapidly as possible, the Japanese government has banned them, while in Europe the tendency has been to control the cellroom environment, perform continuous health checks on the workers by regularly monitoring Hg levels in blood and to carry out careful effluent treatment to remove mercury. It is claimed in the UK that the mercury in effluent from chlor-alkali plants does not significantly increase the mercury level of the local water environment. This diversity of action largely resulted from a difference in the market response to chloride-contaminated sodium hydroxide; European customers insisted on the continued supply of chloride-free sodium hydroxide and diaphragm cells were not able to meet this requirement.

The developments in membrane cell technology have changed the situation markedly. The product quality is, at least, comparable with that from mercury cells and there is no possibility of mercury pollution. Moreover, there are bonuses to the operator in terms of energy consumption and cellroom management. Membrane cells have already largely replaced mercury cells in Japan. In Europe, the performance of the membrane cells is now sufficient and certainly, when combined with pressure from environmental groups, it is probable that all future new cellrooms will be based on membrane cells. In the USA, the predominance of diaphragm cells results from an early switch from the mercury cells and the continued market for weak sodium hydroxide containing chloride ion.



**Table 3.6** An estimate of the split between cell technologies in 1987 (% of total Cl<sub>2</sub> production)

	Mercury	Diaphragm	Membrane
UK	94	5	1
W. Europe	67	27	6
Japan	0	43	57
USA	20	75	5
World	40	50	10

Thus, it is to be expected that the industry will move to membrane cells, although perhaps most slowly in the USA. Two factors retard the change: (1) although there is much pilot-plant and even small-plant experience, there are few very large membrane cell plants in operation and, hence, some suspicion remains about real operational performance; (2) the market for chlorine and sodium hydroxide is not strong enough to demand additional plant, and the driving forces for replacement of existing cellrooms is insufficient until they have reached the end of their natural lifespan. Table 3.6 presents an estimate of the split between the three cell technologies in 1987.

The past 25 years have seen continuous change and improvement in the technology of the chlor-alkali industry. As a result, modern cells are able to produce high purity products while the cell components, designs and control strategies have reached a stage where further improvements in, say, energy consumption, can only be small and will be very difficult to achieve. The only major change which might be envisaged would be a conversion to oxygen cathodes. This, in principle, could reduce energy consumption by a further 60%, but requires the development of catalysts with an acceptable performance and could be achieved only at an expense in terms of more complex cell design because of the need for a gas-fed electrode. Where there is a market for H<sub>2</sub> and, hence, its value influences favourably the process economics, there appears to be no reason to switch to oxygen cathodes. In some circumstances, however, the H<sub>2</sub> can even be a nuisance and then the energy savings from an oxygen cathode look attractive. Indeed, it is believed that some companies now operate large pilot-scale processes using fuel-cell-type cathodes. The oxygen reduction catalyst is dispersed Pt on carbon and the large-area cathodes are constructed from smaller 'tiles' of the porous carbon cathodes.

### 3.4 THE PRODUCTION OF POTASSIUM HYDROXIDE

Potassium hydroxide is considerably more expensive than sodium hydroxide because the feedstock is refined, crystalline, potassium chloride. It is only used when it has a particular advantage, and the production of potassium hydroxide is only 2–3% that the sodium hydroxide. Potassium hydroxide can be produced