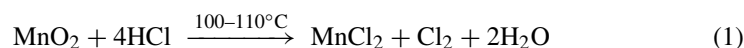


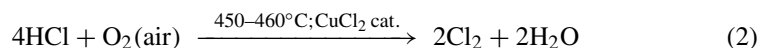
2

History of the Chlor-Alkali Industry

During the last half of the 19th century, chlorine, used almost exclusively in the textile and paper industry, was made [1] by reacting manganese dioxide with hydrochloric acid



Recycling of manganese improved the overall process economics, and the process became known as the Weldon process [2]. In the 1860s, the Deacon process, which generated chlorine by direct catalytic oxidation of hydrochloric acid with air according to Eq. (2) was developed [3].



The HCl required for reactions (1) and (2) was available from the manufacture of soda ash by the LeBlanc process [4,5].



Utilization of HCl from reaction (3) eliminated the major water and air pollution problems of the LeBlanc process and allowed the generation of chlorine. By 1900, the Weldon and Deacon processes generated enough chlorine for the production of about 150,000 tons per year of bleaching powder in England alone [6].

An important discovery during this period was the fact that steel is immune to attack by dry chlorine [7]. This permitted the first commercial production and distribution of dry liquid chlorine by Badische Anilin-und-Soda Fabrik (BASF) of Germany in 1888 [8,9]. This technology, using H_2SO_4 for drying followed by compression of the gas and condensation by cooling, is much the same as is currently practiced.

In the latter part of the 19th century, the Solvay process for caustic soda began to replace the LeBlanc process. The resulting shortage of HCl made it necessary to find another route to chlorine.

Although the first formation of chlorine by the electrolysis of brine was attributed to Cruikshank [10] in 1800, it was 90 years later that the electrolytic method was used successfully on a commercial scale. In 1833, Faraday formulated the laws that governed the electrolysis of aqueous solutions, and patents were issued to Cook and Watt in 1851 and to Stanley in 1853 for the electrolytic production of chlorine from brine [11].

2.1. DIAPHRAGM-CELL TECHNOLOGY DEVELOPMENT

During the electrolysis of NaCl brine, chlorine is generated at the anode and sodium hydroxide is produced at the cathode.

At the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

At the cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$

Overall reaction: $2\text{NaCl} + 2\text{H}_2\text{O} \xrightarrow{2\text{F}} 2\text{NaOH} + \text{Cl}_2 + \text{H}_2$

The main difficulty during the electrolysis of NaCl solutions was that of achieving continuous separation of chlorine generated at the anode and sodium hydroxide produced at the cathode. While it was easy to keep the chlorine and hydrogen gases in U-shaped tubes, the sodium hydroxide formed at the cathode reacted with chlorine to form sodium hypochlorite. The British scientist Charles Watt devised the concept of a current-permeable separator, which allowed the electric current to pass but kept the anode and cathode products separated. Thus, the diaphragm cell was invented in 1851. The major drawback to the use of the Watt cell was the lack of electrical generation capacity. The development of the dynamo around 1865 allowed Edison, Siemens, Varley, Wheatstone, and others to invent generators of electricity with sufficient capacity and efficiency to make electrolytic production of chlorine and caustic soda feasible.

Following the breakthroughs in electricity generation, parallel developments in diaphragm cells were made in many countries. The credit for the first commercial cell for chlorine production goes to the Griesheim Company in Germany, in 1888. This nonpercolating diaphragm cell, used predominantly for Cl_2 production in the early 1900s, was based on the use of porous cement diaphragms, invented by Brauer in 1886 and made by mixing Portland cement with brine acidified with HCl, followed by setting and soaking in water to remove the soluble salts. The cell, termed the Griesheim Elektron cell [12, 13] and shown in Fig. 2.1, consists of an iron box with a steam jacket and is mounted on insulation blocks. Each unit contains six rectangular boxes made of cement about 1 cm thick. The cement boxes act as diaphragms and contain the anodes made of magnetite or graphite. The outer box forms the cathodes, and cathode plates are also provided in the form of iron sheets placed between anode compartments and reach the bottom of the cell. The cell was operated at 2.5 kA, batchwise, with saturated potassium chloride solutions for 3 days until a concentration of 7% KOH was obtained, at a current density of 100–200 A/m² at 80–90°C; the cell voltage is about 4 V and the current efficiency 70–80%. It is very interesting to note that the best operating conditions for this cell were

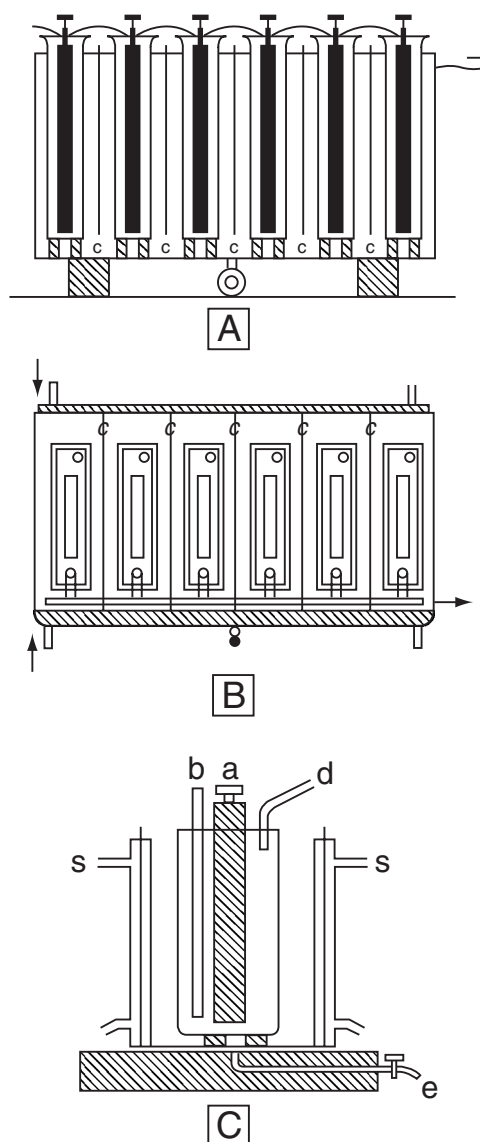


FIGURE 2.1. A and B: Griesheim Elektron cell bank; C: Cross-section of Griesheim Elektron cell. a: anode; b: brine inlet; c: cathode; d: brine outlet; e: caustic outlet; s: steam.

found to be: (1) anodes preferably of magnetite, to obtain pure chlorine without any CO_2 in the anode gas, (2) high concentration of brine, and (3) a temperature of $80\text{--}90^\circ\text{C}$, to reduce the cell voltage. Items (2) and (3) are still the desired parameters for optimal cell operation.

The first diaphragm cell developed in Great Britain was the Hargreaves–Bird cell, operated in 1890 by the United Alkali Company. Each cell consisted of a rectangular iron box lined with cement. The box was 10 ft long, 4–5 ft deep, and 2 ft wide, divided into

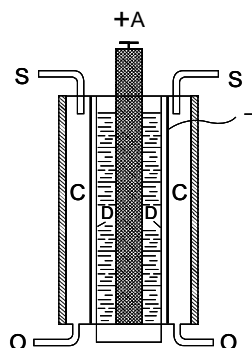


FIGURE 2.2. Hargreaves–Bird cell. A: anodes; C: cathodes; D: diaphragms; O: outlet pipes for brine mixed with sodium carbonate; S: outlets for CO_2 and steam.

three parts of two separate asbestos sheet diaphragms. Six carbon anodes were placed in the anode compartment, and the cathode was a copper gauze attached to the diaphragms. This basic approach of anchoring the diaphragm onto the cathode is still used in modern diaphragm cells. The cell design is shown in Fig. 2.2.

The anode compartment was filled with saturated brine, and during electrolysis chlorine evolved at the anode. The sodium ions, along with sodium chloride and water, percolated through the diaphragm into the cathode compartment. Back migration of hydroxyl ions was suppressed by injecting CO_2 and steam into the cathode compartment to form sodium carbonate. The major contribution of this cell was its vertical diaphragm configuration, which is the basis of modern cells.

Twelve cells were run in series at 2 kA, which corresponds to a current density of 200 A/m^2 , at 4 to 4.5 V, when 60% of the salt is converted to sodium carbonate.

The cell, used in France and Italy, was the Outhenin–Chalandre cell [13], which consisted of an iron box divided into three compartments; the outer ones contained the cathode liquor, and the inner one had the graphite anodes in strong brine. The diaphragm was made from cylindrical unglazed porcelain tubes, cemented together into dividing walls of the cell. This cell was more complex than the Griesheim cell and required considerable attention.

In the United States, LeSueur [14–17] developed and operated a cell in 1890, employing a percolating horizontal diaphragm (Fig. 2.3A). This design permitted brine to flow from the anolyte through the diaphragm continuously to achieve a higher efficiency than the contemporary nonpercolating diaphragm cells in Germany and Great Britain. LeSueur's percolating diaphragm cell, which is the basis for all diaphragm chlor-alkali cells in use today, shown in Fig. 2.3B, is an improved version of the cell depicted in Fig. 2.3A.

The LeSueur cell was made of iron and divided into two compartments separated by a diaphragm, which was deposited on an iron-gauze cathode. The anode was graphite, and the anode compartment was sealed to avoid the release of chlorine. The liquid level in the anode compartment was higher than the level in the cathode compartment, and the caustic flowed out of the cell continuously. This was the first cell to use the percolation method for caustic withdrawal.

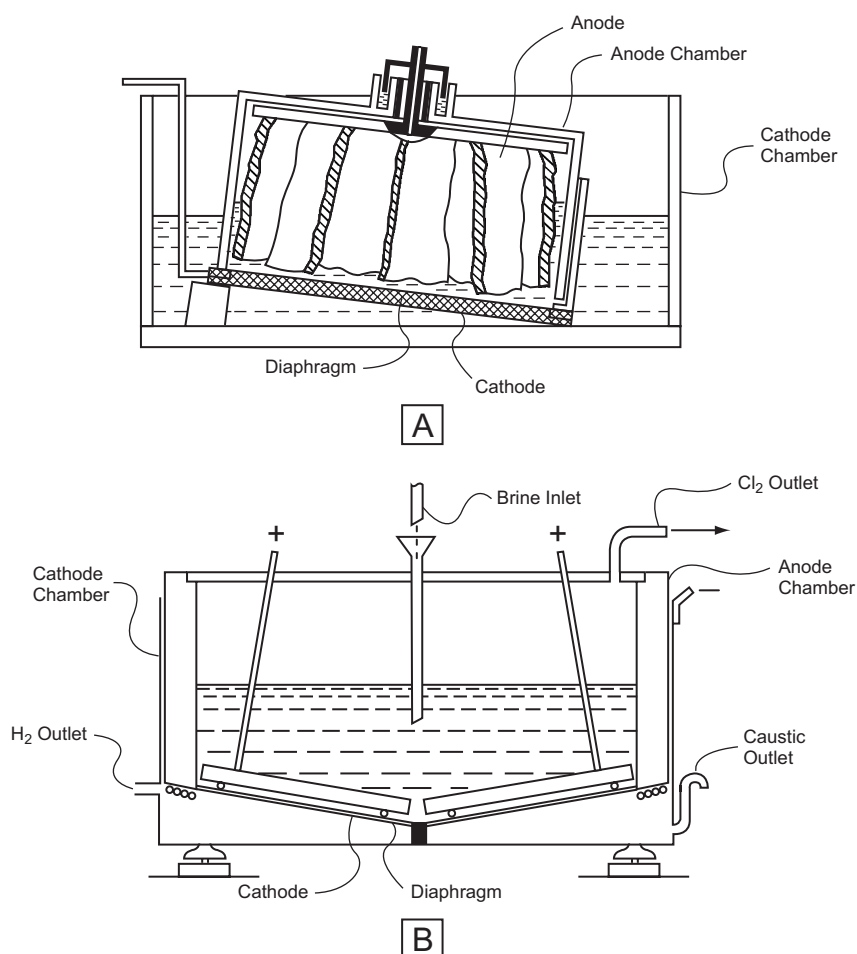


FIGURE 2.3. A: original LeSueur cell; B: modified LeSueur cell.

During the 1920s, the Billiter cell was developed in Germany [13]. This cell was similar to the LeSueur cell, and the original design had a flat electrode and a horizontal diaphragm. By modifying the cathode to a corrugated shape, current loads were increased from 12 kA to 24 kA (Figs. 2.4A and B). The diaphragm was a closed woven steel screen covered with a mixture of long fiber asbestos wool and barium sulfate. Asbestos became the primary component of the diaphragm for the next 80 years.

There was significant cell development activity during the period 1890–1910, following LeSueur’s and Hargreaves–Bird cell with a vertical diaphragm, and the development of synthetic graphite independently by Castner and Vaughn, and Acheson [18], who also developed a method for producing synthetic graphite anodes. The cell designs focused on heavy concrete housing, either cylindrical or vertical, with graphite anodes entering through the top and the cathode plates bolted on the side. The basic types of

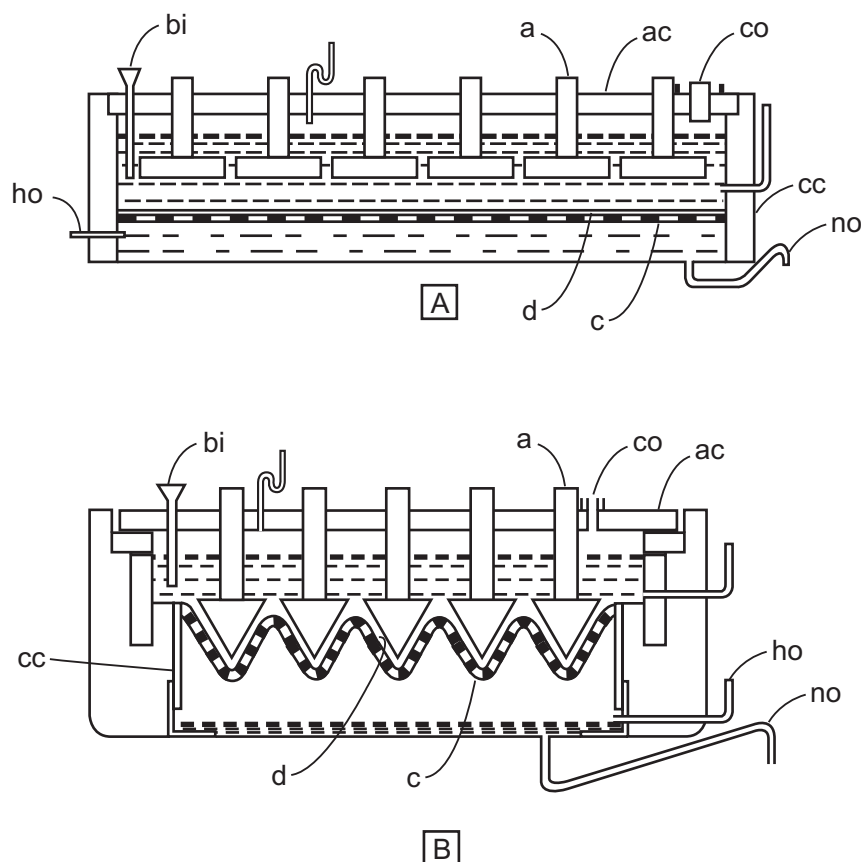


FIGURE 2.4. Billiter cell. A: flat cathode; B: corrugated cathode. a: anode; c: cathode; d: diaphragm; ac: anode chamber; cc: cathode chamber; bi: brine inlet; co: chlorine outlet; no: caustic outlet; ho: hydrogen outlet.

cells developed were rectangular vertical cells, cylindrical cells, and bipolar filter-press type cells, as shown in Fig. 2.5.

2.1.1. Vertical Diaphragm Cells

Of the various vertical diaphragm cells shown in Fig. 2.5, the Townsend cell was the forerunner of the modern diaphragm cells. The cell design of the early 1900s had poor efficiency as the chlorine was reacting with the back-migrating caustic. This problem was addressed in the Townsend process by covering the caustic with a film of kerosene. The first plant employing the Townsend cell was built in Niagara Falls, and had 68 2-kA cells, producing chlorine and caustic soda with low hypochlorite and chlorate. One of the important developments that took place around this period was feeding the saturated brine through orifices to maintain the desired brine level in the cell, thereby eliminating expensive overflow controls [19].

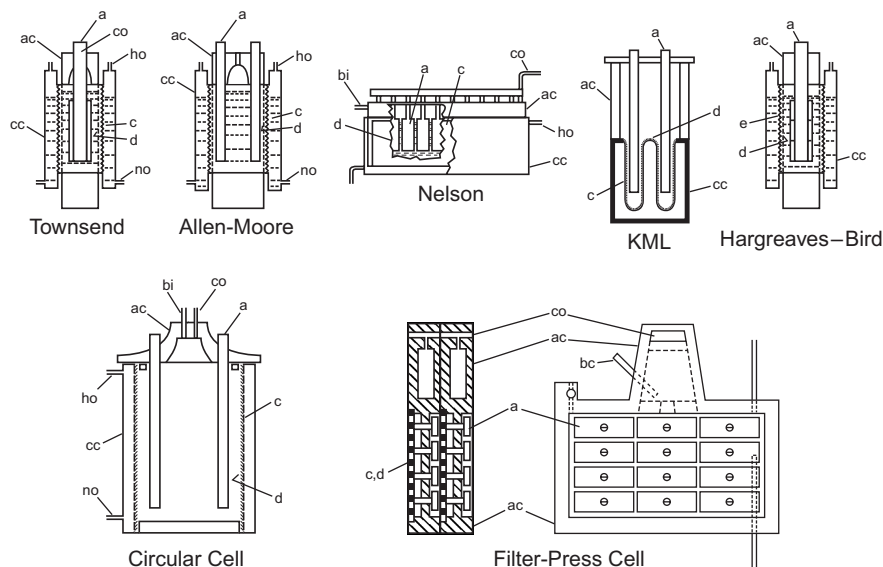


FIGURE 2.5. Schematic of historical diaphragm cells. The symbols are the same as in Fig. 2.4.

Clarence Marsh improved the design of the Townsend cell in 1913 by installing side-entering cathodes and anodes and corrugated finger cathode plates. This design was the forerunner of the cathode used in Hooker Type S cell with asbestos paper folded to fit the corrugations, the edges being protected by putty. However, the cell putty disintegrated exposing the bare cathode surface and thereby reducing the cell current efficiency. In 1925, Stuart solved the problem of completely covering the round cathode pieces by mixing asbestos fiber in dilute caustic liquor and sucking the asbestos mixture onto the cathode by applying a vacuum. The asbestos then formed a tight coating on the cathode, conforming perfectly to the contours of the cathode figures. This technique of vacuum deposition of asbestos is one of the most important developments in the history of chlor-alkali cells [19]. The Marsh cell, before and after diaphragm deposition, is shown in Fig. 2.6.

Following the invention of deposited asbestos diaphragms, Stuart developed the Hooker “S” cell, which had vertical cathode fingers with deposited diaphragms. These “S” cells were very popular after World War II and were phased into operation throughout the world. In 1960, almost 60% of the chlorine production in the United States was in Hooker cells.

While Hooker pioneered the development of vertical diaphragm cells, Diamond Alkali Company developed an alternate cell design. In 1959, Diamond licensed a cell with cathode fingers, which run continuously from one side of the cell to the other. The support of the cathode fingers at both ends (as opposed to Hooker’s cantilevered construction with support only at one end) helped ensure the stability of anode–cathode alignment. Also, the fingers are oriented parallel to the cell circuit to accommodate thermal expansion during operation, and realize voltage savings via the reduced current path. This feature

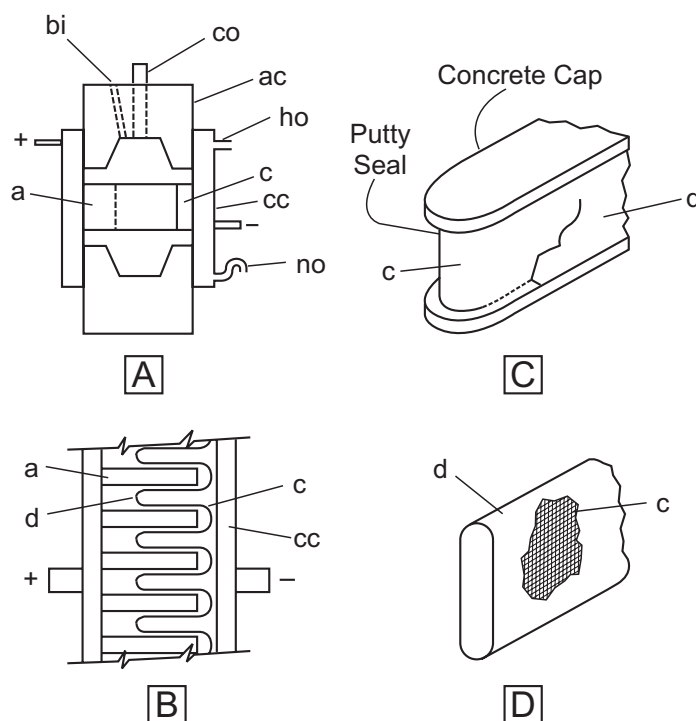


FIGURE 2.6. Marsh cell. A: vertical section; B: plan, sectional diagram; C: original cathode with asbestos paper diaphragm; D: asbestos deposited cathode finger. The symbols are the same as in Fig. 2.4.

has been adopted in almost all modern cells including some Hooker types described in Russian patents. The alternative cathode finger supports are shown in Fig. 2.7.

2.1.2. Developments in Anodes and Diaphragms

During the early 1900s, the anode used for chlorine generation was either platinum or magnetite. However, because of the high cost of platinum and the current density limitation (0.4 kA/m^2) with the magnetite, graphite became the predominantly used anode material from 1913 to the mid-1970s.

Artificial graphite anodes were developed by Acheson and, in 1919, Wheeler improved their performance by impregnation with linseed oil. Periodic replacement of anodes was nevertheless necessary, as the graphite blades wore away resulting in higher cell voltage, due to the increased anode–cathode gap. This motivated the search for dimensionally stable anode structures to replace graphite. Platinum and Pt/Ir activated titanium was found to offer excellent corrosion resistance in brine electrolysis service. However, these anodes suffered from either a short life or a high cost.

Henri Bernard Beer developed and applied for two patents [20] issued in 1965 and 1967 that revolutionized the chlor-alkali industry. These patents described thermal decomposition techniques to coat titanium substrates with mixed crystals of valve metal

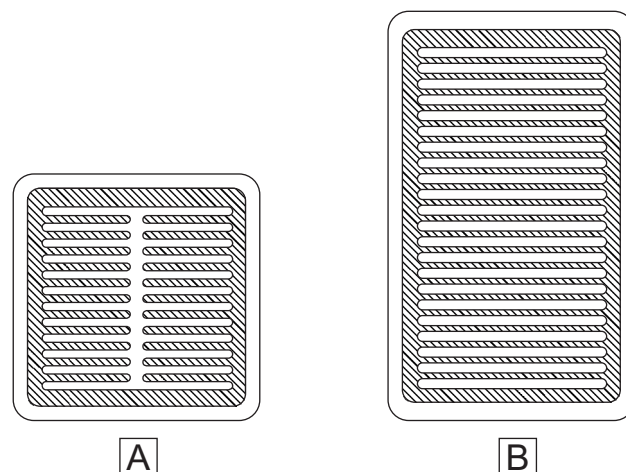


FIGURE 2.7. Comparison of Hooker and Diamond cathode designs. A: finger type construction (Hooker type “S” cell); B: flattened tube-type construction (Columbia-Hooker Diamond, Hooker type “T”).

oxides and platinum group metal oxides—the valve-metal oxide content in these coatings being more than 50%. These anodes were initially used in DeNora mercury cells, and they exhibited low cell voltage and a long life. Over the next few years, most diaphragm-cell plants throughout the world were converted to these anodes, which were given the registered trademark DSA[®], for dimensionally stable anodes [21]. All the technology suppliers, to realize the benefits of the low energy consumption offered by the metal anodes, changed their cell configurations to incorporate the metal anode.

After the development of dimensionally stable anodes, the focus shifted to improvements in asbestos diaphragms. Replacement of concrete tops with fiberglass-reinforced polyester cell tops improved diaphragm life and voltage by eliminating the degradation products of concrete. Still, the asbestos diaphragms swelled during operation, resulting in increased cell voltage. Diamond Shamrock examined the behavior of these asbestos diaphragms and developed a modified composition by mixing asbestos and polytetrafluoroethylene (PTFE), which, on heating, resulted in a dimensionally stable diaphragm [22]. This diaphragm showed improved cell voltage in commercial tests in 1972, and made possible the use of expandable anodes, also developed by Diamond [23]. At the same time, Hooker developed a stabilized diaphragm, HAPP (Hooker Asbestos Plus Polymer), which did not swell. This diaphragm was formed by mixing a polymer into the asbestos slurry before deposition and baking at the fusion point of the polymer [24].

A major concern with continued exposure to asbestos is its toxicological effect on the human body resulting in diseases—such as asbestosis, which becomes significant 15 to 20 years after first exposure. As a result, the EPA has banned its use in roofing felts, flooring felts, vinyl-asbestos floor tile, asbestos cement pipe and fittings, and heat-resistant clothing. Although the chlorine industry in the USA is currently exempt, allowing continued use of asbestos as diaphragm material, it is believed that environmental pressures will ultimately force the industry to adopt non-asbestos diaphragm technology. Some

countries have already banned asbestos or defined preferred technology as asbestos-free. Anticipating the potential replacement of asbestos, there has been a flurry of activity to develop non-asbestos diaphragms. These include the microporous diaphragm, which is either a PTFE sheet containing sodium carbonate as a pore former [25] or a mixture of PTFE fibers and zirconia [26], vacuum-depositable non-asbestos fibers called Polyramix [27] and Tephram [28]. Details related to these technologies are addressed in Section 4.7.

2.1.3. Diaphragm-Cell Technologies

As mentioned previously, the vacuum-deposited diaphragm developed in 1928, coupled with the vertical finger anode–cathode construction, initiated the Hooker “S” series cell. The “S” type cell continued until 1966, when the single C-60 cell was introduced. In 1970, the “H” series cell was introduced, with metal anodes replacing the graphite anodes. A summary of the major innovations in Hooker diaphragm-cell design is presented in Table 2.1.

Diamond Alkali developed cells very similar to the Hooker cells and began licensing the technology in 1959. Its main cell during the late 1950s and the early 1960s was the D-3 cell operating at 33 kA. As noted earlier, the D-3 had cathode fingers secured on both sides of the cathode assembly, which was a rectangular steel can with a

TABLE 2.1. Summary of Major Changes in Hooker Diaphragm Technology

Date	Cell	Key innovation
1928–48	S-1	First successful deposited diaphragm cell. Consistent increases in the allowable amperage with minor electrical circuit changes
1948	S-3	Doubled the anode and cathode areas of S-1 to double capacity
1951	S-3A	Conductor sizes increased to permit greater current density
1956	S-3B	Increased Cl_2 and H_2 disengaging space to permit greater chlorine production
1960	S-3C	Redesigned conductors for optimum economic current density
1963	S-4	Increased anode and cathode height and added five rows of electrodes over S-3C to increase cell output
1964	S-4B	Decreased grid height to decrease cost without affecting cathode area. Disengaging space increased accordingly
1966	C-60	Redesigned cathode to reduce copper content without increasing voltage
1970	H-1	Substituted metal anodes for graphite anodes in S-4B to increase current density and cell life
1970	H-2, 2A	Increased cathode and base copper to carry large currents on basic S-4 and C-60 designs
1971	HC-4B	Substituted metal anodes for graphite anodes in S-3C to increase current density and cell life
1972	H-4	Increased anode and cathode area to increase capacity
1978	H-4M	Added polymer to asbestos to create a stable, resistant diaphragm with reduced energy consumption
1979	H-4/84 (or LCD)	The LCD (low current density) cell operated with about 12% lower current density by reducing the anode–cathode gap, and allowing for more anode and cathode fingers in the shell of the H-4 cathode

deposited asbestos diaphragm. A concrete head on top of the cathode assembly completed the cell.

Later models of Diamond cells include the DS-31, DS-45, and DS-85, which used metal anodes. The DS-85 model allows amperage up to 150 kA. The base or cell “bottom” features a patented design consisting of a welded steel structure supporting a flat copper grid, which carries current to the anodes. A corrosion-resistant mat covers the grid to protect the copper from attack by the anolyte and the vertically disposed metal anodes are simply bolted to the base through the mat. As in Hooker designs, the cover or cell head is made of proprietary polyester resin instead of concrete. This type of cover avoids the anolyte contamination resulting from attack on the concrete (as experienced in earlier cells), and this, in turn, reduces the frequency of blockage of the diaphragm.

ELTECH System Corporation currently markets both the Hooker cells and Diamond cells. Other diaphragm-cell technologies developed during the 1970s include the Hooker–Uhde cell and the ICI–Solvay cell. These cell designs are addressed in Chapter 5.

2.1.4. *Bipolar Diaphragm Cells*

The filter-press cell for producing chlorine and caustic was designed by several early investigators. However, it was Dow who pioneered the development of bipolar filter-press cells over several years in view of the advantages, which included minimization of the bus between the cells and floor space, and low capital cost. The original patents of Dow were issued in 1911 and 1913 [29]. The filter-press cell design, patented in 1921 [30], shown in Fig. 2.5, comprises concrete filter-press units with graphite rods embedded and extending into the anode compartment, and the cathode screen on the other side.

An improved bipolar design of Dow is described in U.S. patent 2,282,058 (1942) by Hunter-Otis and Blue, where a graphite dividing wall was cast into the concrete filter-press frame with graphite anodes projecting vertically from the backing plate. The cathode fingers were made of steel wire screen wrapped with asbestos paper and fastened to a screen backing plate of the adjacent unit cell. Lucas and Armstrong [31] made additional improvements to this cell by using bipolar units, which slip into grooves in a cell box, which eliminated the sealing problems. The cathode fingers of steel wire screen and graphite anodes project vertically from a steel base plate, thereby constituting an integral electrode unit. Figures 2.8 and 2.9 describe the cell designs of Hunter-Otis and Blue, and of Lucas and Armstrong. These cells have been modernized with metal anodes and modified diaphragms in recent years.

PPG and DeNora jointly developed a bipolar filter-press diaphragm cell called the Glanor[®] electrolyzer [32]. The central design feature is the bipolar electrode where one side acts as an anode and the other as a cathode. The electrode consists of a steel plate to which anode fingers are connected on one side and cathode fingers on the other.

The electrode is set into a bipolar element, which consists of a channel frame surrounding the anodes, lined with titanium for protection against corrosion in the anolyte environment. The elements, with the anode side of one facing the cathode side of another, thereby forming a cell, are clamped together with tie-rods. The resulting assemblage has the appearance of a plate and frame filter-press—a commonly used piece of equipment for filtration operations. Hence, the term “bipolar filter-press cell.”

Bipolar cell designs and their performance characteristics are discussed in Chapter 5.

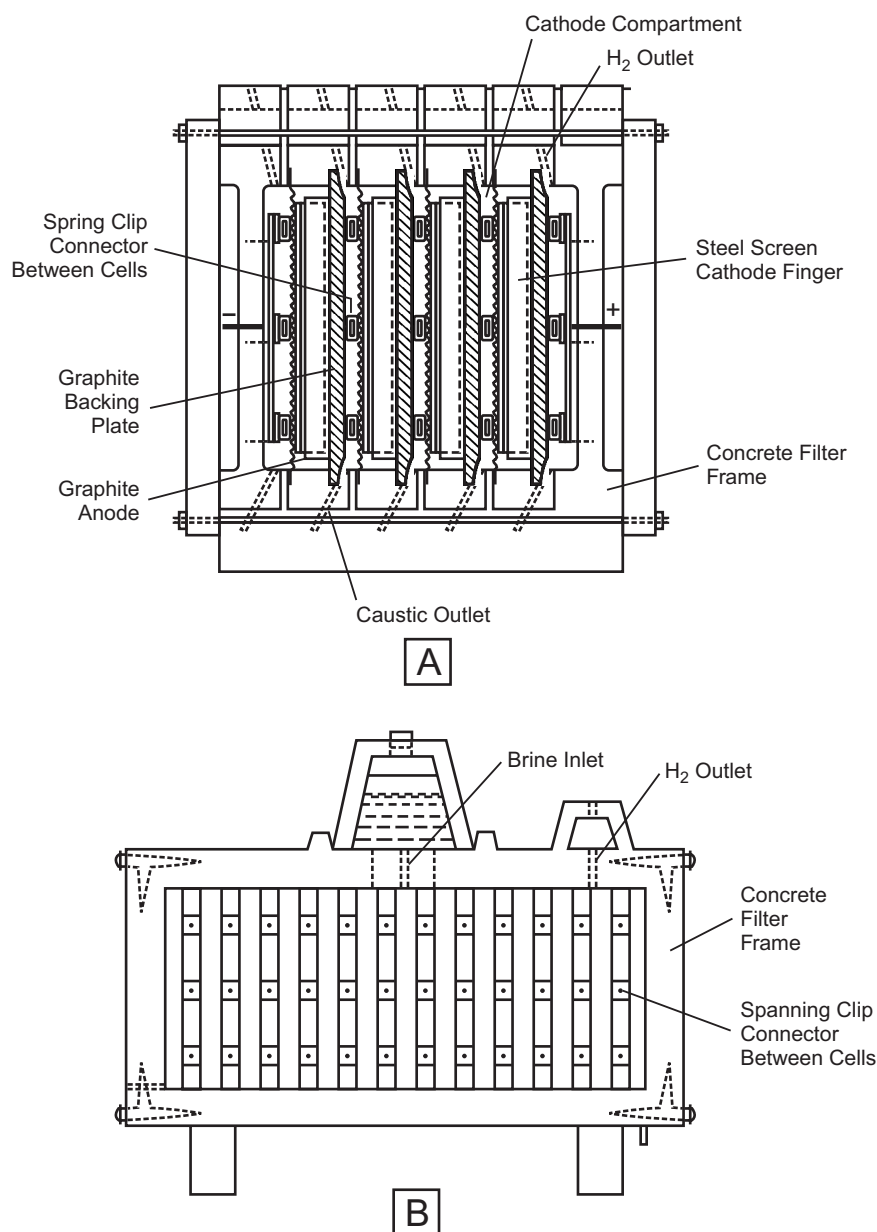


FIGURE 2.8. Dow filter-press cell of Hunter-Otis and Blue. A: basic cell configuration; B: horizontal cross-sectional view.

2.2. MERCURY-CELL TECHNOLOGY

An alternative method of producing chlorine and caustic soda involves the use of mercury cells, whose cathode reactions differ from those occurring in diaphragm cells.

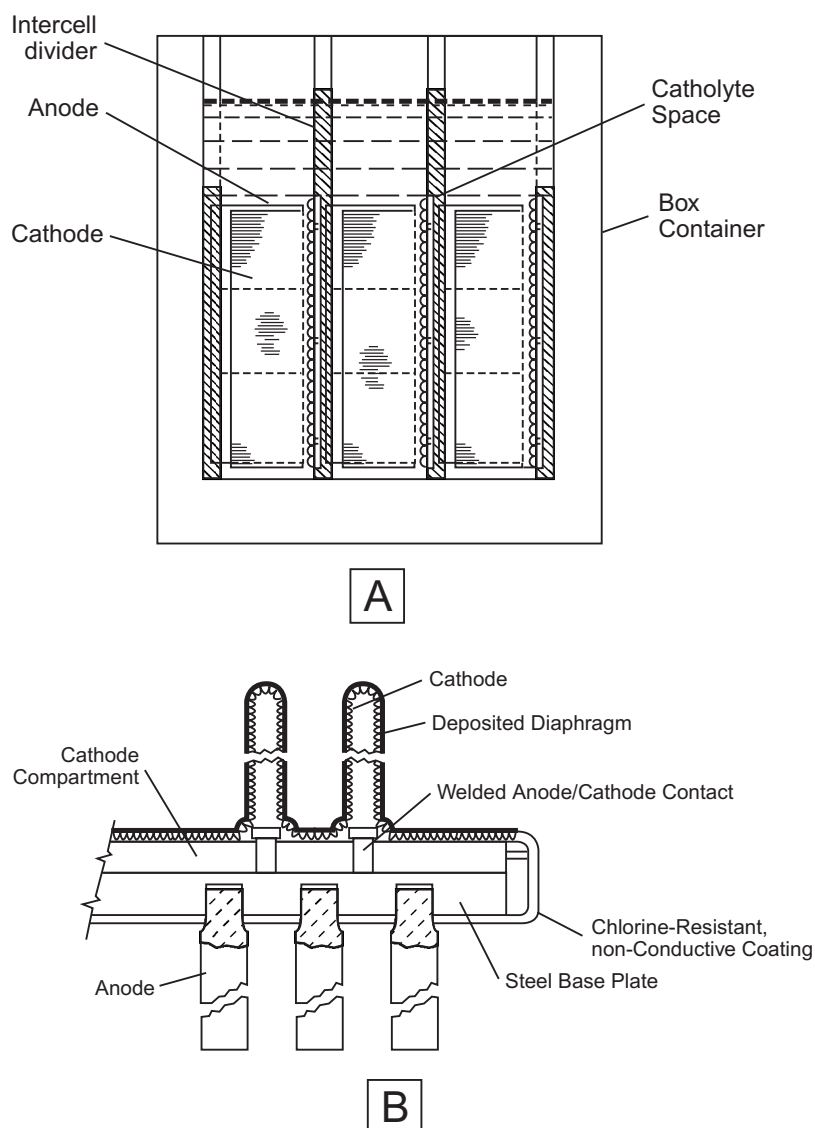
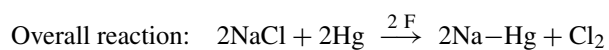
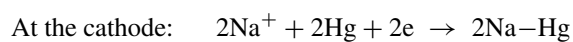
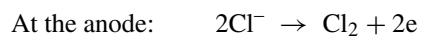


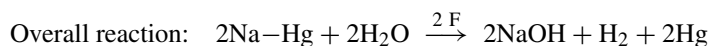
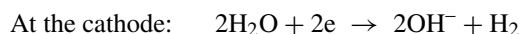
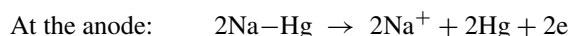
FIGURE 2.9. Dow box cell of Lucas and Armstrong. A: Dow box cell; B: horizontal section of bipolar electrode.

The mercury cell consists of two primary units—the electrolyzer and the decomposer or denuder. The principal electrochemical reactions are as follows:

In the electrolyzer:



In the decomposer:



The overall process involves a flow of purified, saturated brine through an elongated, slightly inclined trough between a shallow cocurrent stream of mercury and an assembly of electrodes (graphite or metal), the lower surfaces of which are close to the mercury surface and parallel to it. The cell trough is provided with a gas-tight cover, which also serves to support the anodes. During electrolysis, chlorine is liberated at the anodes, while the sodium ions are discharged at the surface of the mercury cathode to form a low concentration sodium amalgam (0.10–0.30% sodium by weight). Thus, the sodium ions are almost entirely prevented from reacting with the aqueous electrolyte to form caustic soda, or with dissolved chlorine to re-form sodium chloride. The amalgam reacts with water in the decomposer to form pure concentrated caustic.

The mercury-cell process for producing chlorine and caustic was developed by Hamilton Y. Castner, an American, and Karl Kellner, an Austrian, in 1892, although the first patent dealing with mercury cell was British patent 4349, issued in 1882, to Nolf. Following patent disputes, Castner and Kellner combined their efforts and sold their combined patent rights to Solvay et Cie. The first mercury cell of Castner consisted of a stationary, thick cast-iron base in which cylinders were bored for the ram pumps employed to circulate the amalgam. There were two anode compartments for electrolysis and an intermediate compartment for amalgam decomposition to generate caustic. This cell suffered from seizure of the ram pumps, as a result of the growth of caustic soda deposits. Castner overcame the problem of pumping mercury by using a rocking cell (Fig. 2.10), which was built in 1894 in England. A similar plant was built in 1895 in

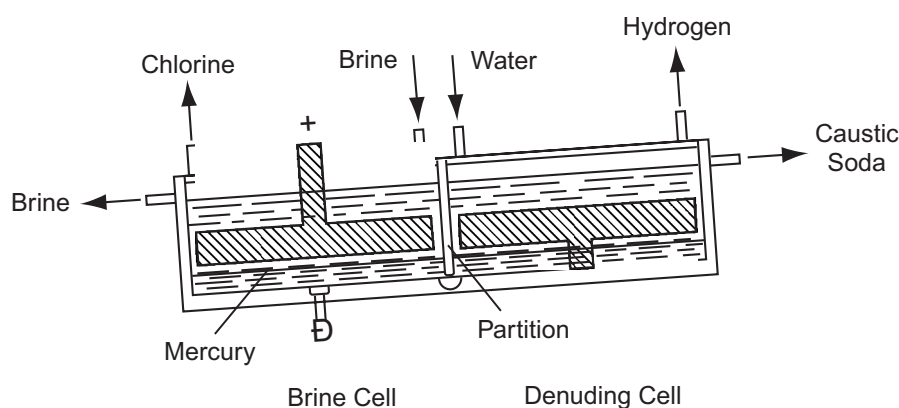


FIGURE 2.10. Schematic of original mercury cell.

Saltville, VA, and the Mathieson Alkali Company adopted this process in 1897. The Castner–Kellner Alkali Company started production in Weston Point, Runcorn, in 1897, and the Mathieson Alkali works began production in the same year at Niagara Falls.

The success of the latter venture was evidenced by the fact that the capacity of the plant was greatly enlarged, and except for minor changes, the old Castner “rocking cells” were in continuous operation from 1897 to 1960 [33]. They were finally replaced by 100 kA Olin Mathieson cells.

Parallel to this development in the United States, Brichaux and W. Wilsing of Solvay built the first “long” cell, in Germany, in 1898. This cell had the modern characteristics of forced mercury circulation.

With the growth of synthetic fibers, such as rayon, a tremendous demand for very pure (salt free) caustic soda developed. A significant number of mercury-cell plants were built in the years around World War II.

Cell capacities increased progressively after 1945, from about 10 kA to 200–300 kA. Suppliers of this technology include De Nora, Hoechst–Udde, Krebs, Krebskosmo, BASF, Kureha, Olin–Mathieson, Solvay, Toyo Soda, and Asahi Glass. The increased capacity of the mercury cell depended on the use of efficient silicon rectifiers, which replaced the old mercury-arc rectifiers. The distinguishing differences in these mercury-cell technologies lie in several design factors which include the manner by which mercury is fed to the electrolyzer (e.g., gravity flow vs forced flow), decomposer design, support structure for the anodes and the cathodes, types of cell cover, and mercury inventory requirements, the main motivation being improved economics. These technologies are outlined in Chapter 5.

The primary cell technology used for producing chlorine and caustic, in the world and in United States, is the diaphragm-cell process, which had a 37% share of world chlorine production. In the United States, the diaphragm cell contributed 67% of chlorine production [34]. The mercury-cell technology had a dominating share initially. However, following the mercury poisoning cases in Minamata and Niigata, both in Japan, in 1972, there has been a declining trend away from this technology for chlorine production. Japan was the first country to change from mercury-cell technology, and currently there is no mercury-cell operation in Japan. In Western Europe, mercury-cell technology is more widely practiced. The mercury-cell technology still accounts for 18% share in 2001, in the world. Mercury cells generate 11% of the chlorine produced in the United States. This situation is unlikely to dramatically change in the near future. The environmental issues and concerns related to the mercury-cell process are discussed in Chapter 16.

2.3. MEMBRANE-CELL TECHNOLOGY

An alternative to diaphragm and mercury cells is the membrane cell. Actually, the membrane cell is a modification of the diaphragm cell wherein the diaphragm is replaced with a permselective ion-exchange membrane. The membrane inhibits the passage of negative chloride ions but allows positive sodium ions to move through freely.

In the membrane-cell process, sodium or potassium chloride brine is fed to the cell and distributed equally among the anode compartments, while water fed into a second header flows into the cathode compartments or into an externally recirculating stream

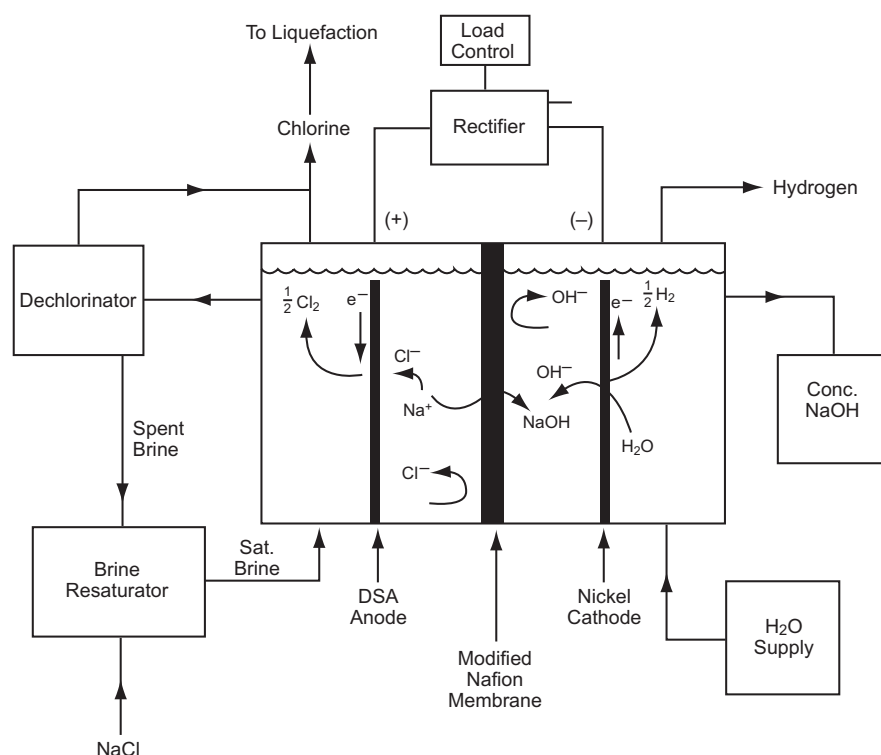


FIGURE 2.11. Schematic of ion-exchange membrane cell. (Reproduced with permission of the Society of Chemical Industry.)

of catholyte. The electrode reactions are the same as in a diaphragm cell. The depleted brine, or anolyte, overflows with the chlorine gas into an anolyte header and the caustic soda liquor overflows with the hydrogen gas into a catholyte header. Figure 2.11 is a schematic diagram of the membrane-cell process.

Several firms participated in the development of the membrane cell. Conceptual studies of permselective membranes began in the mid-1940s. W. Juda *et al.* of Ionics Corporation, and S.G. Osborne of Hooker Chemical hold early patents (1950s) on the membrane-cell process [35].

Diamond and Ionics mounted a joint effort to develop the membrane cell from the mid-1950s to the early 1960s [36]. This work demonstrated the feasibility of the concept, but serious problems developed, including erosion of carbon anodes, high cell voltage, and very short membrane life. The project was dormant for about 10 years.

In the late 1960s, concern over environmental problems associated with mercury-cell plants initiated a revival of interest in the membrane-cell technology. Initial problems associated with membrane cells were steadily being alleviated in the early 1970s. The development of metal anodes negated problems associated with graphite anode erosion. As a spin-off of the space program, DuPont developed a perfluorinated ion-exchange

membrane while performing fuel cell research. This membrane was initially called “XR” and was later trademarked as “Nafion.” Nafion® membranes were found to have good ion-exchange properties as well as high resistance to the harsh environment of the chlor-alkali cell.

After DuPont introduced Nafion® membranes, Diamond Shamrock intensified its research efforts in membrane-cell technology. Initial research tests with the membranes began in 1970 using laboratory cells. In 1972, a commercial-size electrolyzer and pilot plant were placed in operation in Painesville, Ohio. Four years later, a 20-ton per day demonstration plant was built in Muscle Shoals, Alabama. This unit was integrated with an existing mercury-cell plant.

Diamond’s first commercial membrane cell was its “DM-14 Electrolyzer,” a monopolar cell. A number of individual membranes are held between anode and cathode frames bolted together in a “filter-press” configuration. Each electrolyzer unit (anode, membrane, and cathode) has an active electrode area of 1.41 m^2 . A current density of 3.1 kA/m^2 produces 0.14 metric ton of caustic per unit per day. The number of unit cells bolted together determines the operating amperage of the electrolyzer, ranging from 5 kA to over 150 kA. Because of the monopolar arrangement of the cells, the voltage of the electrolyzer is independent of the number of membranes installed in the electrolyzer [36]. The DM-14 operated at 3.9 V at a current density of 3.1 kA/m^2 .

Like Diamond, Hooker Chemicals demonstrated an interest in ion-exchange membranes since the mid-1940s. S.G. Osborne *et al.* of Hooker Chemical Corporation hold the original patent for the first membrane cell [36]. This patent was filed on January 23, 1952. With this patent, Hooker embarked upon a major development program until 1957. Following a period of relative inactivity, the Nafion® membrane rekindled interest in membrane-cell technology.

Research during the early 1970s culminated in the licensing of the MX cell of Hooker Chemicals to Reed Paper Ltd., a firm that built a 45-ton per day membrane plant at Dryden, Ontario. Actually, these membrane cells replaced 13-year-old mercury cells that were being phased out because of growing concern over mercury pollution problems in Canada. The plant was brought on stream on November 19, 1975.

Around the same period, Asahi Chemical started a pilot plant operation with ion-exchange membrane cells, using DuPont’s Nafion®. In 1975, a commercial plant was commissioned, producing about 10 tons of caustic/day, at Nobeoka in Japan.

Since then, several membrane-cell technologies were developed in Japan, as a pollution-free chlor-alkali process. Japanese contributions include composite membranes and several electrolyzer designs. Japan was the first major chlorine producing country to convert entirely to membrane cell technology. As of January 2003, ~35% of world production of chlorine is by membrane-cell technology, generating ~52,000 metric tons caustic/day.

Many chlor-alkali producers and technology licensing companies have refined and optimized membrane cell designs to realize low energy consumption and long life. The new cell designs incorporated the zero-gap concept, which eliminated the electrolyte gap between the electrodes and the membrane.

Two types of electrolyzers were developed, and are labeled monopolar or bipolar. In the monopolar type, all of the anode and the cathode elements are arranged electrically in

parallel, constituting an electrolyzer operating at high amperage and low voltage. In the bipolar type, the cathode of a cell is connected to the anode of an adjoining cell, so that the cells are in series and the resulting electrolyzer has low amperage and high voltage. The advantages and disadvantages associated with these electrolyzer configurations are addressed in Chapter 5.

Membrane-cell technologies were developed for licensing by Asahi Chemical Industry, Asahi Glass, Chlorine Engineers, ICI, Lurgi, DeNora, Uhde, ELTECH, PPG, and Tokuyama Soda. Presently, there are only five major suppliers of cell technology and they are: Asahi Kasei Corporation (Asahi Chemical Industry), Chlorine Engineers, ELTECH Systems Corporation, INEOS Chlor (formerly ICI), and Uhde. Chlorine Engineers Corporation still makes available the technology of Asahi Glass, and Uhde and DeNora have combined their technical efforts. The performance characteristics and the distinguishing features in these cell technologies of the bipolar and monopolar type are discussed in Chapter 5.

Another development worth noting was the diaphragm retrofit technology, where ion-exchange membranes replace the asbestos diaphragms in an existing cell. During the retrofitting operation, the membranes are shaped and heat sealed to cover the electrodes, thereby replacing asbestos. Chlorine Engineers applied this approach to the DS cells and Kanegafuchi Chemical to H-series cells [37]. The diaphragm retrofit technology was proven by several companies, including Mitsui Chemical, Tokuyama Soda, and Toyo Soda [38,39].

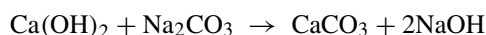
The first membranes, made from the perfluorosulfonate polymer Nafion[®] [40–42], were practical only at low caustic concentrations, as the caustic efficiency decreased significantly at high caustic strengths. To overcome this problem, asymmetric membranes having sulfonic acid groups on the anode side and converted groups on the cathode side were developed. Later, a perfluorocarboxylate membrane, Flemion [43], which exhibited better resistance to caustic back-migration was produced. The low electrical resistivity of persulfonate-based membranes and the low caustic back-migration characteristics of perfluorocarboxylate membranes were coupled by converting the sulfonic acid groups of Nafion[®] to carboxylate groups on the cathode side to realize the beneficial properties of both the membrane types. Today's membranes comprise a perfluorosulfonate polymer layer, a PTFE reinforcing fabric and a perfluorocarboxylate polymer, all bonded together. The performance of these composite membranes is discussed in Section 4.8.

2.4. CAUSTIC SODA

In the early 1900s, caustic soda was manufactured by the lime-soda process (Section 2.4.1), even when caustic was available from the chlor-alkali electrolysis process, as there was not much demand for chlorine. During World War I, chlorine demand dramatically increased to provide chlorine for the production of various chemicals. This led to an increased share of the market for caustic from the electrolytic process. World War II had a similar effect. Nowadays, nearly all caustic soda is a coproduct of electrolytic chlorine.

2.4.1. Lime Soda Process

This process involves reaction of lime with sodium carbonate as follows:



Calcium carbonate precipitates from the calcium hydroxide solution, as it has a lower solubility than that of calcium hydroxide. The optimum reaction temperature is 80 to 90°C. The calcium carbonate is settled, and the overflow is a weak caustic soda, which is concentrated by evaporation.

2.4.2. Electrolytic Process

Caustic soda is produced as a coproduct of chlorine in the sodium chloride brine electrolytic process employing diaphragm cells, mercury cells, and membrane cells.

The diaphragm cell produces caustic soda containing 11% caustic soda and 15% salt, with a low concentration of sodium chlorate. This solution, called cell liquor, is evaporated to produce 50% caustic soda. During evaporation, salt crystallizes as the caustic concentration increases. About 1% salt is present in the 50% caustic soda solution.

The mercury cell produces 50% caustic, and it can also produce up to 70% caustic soda. This is a highly pure caustic with a few ppm of salt and less than 5 ppm of sodium chlorate. However, it carries trace amounts of mercury, and hence, many customers do not accept the caustic soda from mercury cells.

The membrane cell produces about 35% caustic soda, which is concentrated by evaporation to 50%. Membrane cell caustic soda is the preferred product compared to the diaphragm and mercury-cell caustic soda.

2.5. FUTURE DEVELOPMENTS

Significant studies were made in the chlor-alkali technologies during the last century to economically and optimally produce chlorine and caustic soda in an environmentally safe manner, complying with all government regulations. The energy consumed has decreased from about 4,000 AC kWh/ton of caustic in the 1950s to about 2,500 AC kWh during 1998 with the advent of the dimensionally stable anodes and optimal cell design/operation. Additional improvements such as the incorporation of fuel cell concepts and electrocatalyst development, will further reduce the energy consumption and hence, the cost for producing chlorine and caustic.

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