CHLORINE

1. Introduction

Chlorine and caustic soda, manufactured by the electrolysis of aqueous sodium chloride (or brine), are among the top ten commodity chemicals, in terms of capacity, in the United States. When chlorine is produced electrolytically, caustic soda is also produced in a ratio of 1.1 units of caustic soda per unit of chlorine. The combination of 1 ton of chlorine and 1.1 tons of caustic soda generated in this process is referred to as an electrochemical unit (ECU). Since one molecule cannot be created in this process without the other, profitability, costs, and margins are evaluated on an ECU basis in the chlor-alkali industry (1–7).

There are, however, chlorine processes that do not produce caustic soda, such as the electrolysis of hydrogen chloride. A small amount of chlorine is produced in conjunction with molten metal, such as sodium and magnesium, and by the electrolysis of potassium chloride solutions to generate potassium hydroxide (KOH).

Almost all new grassroots capacity will utilize membrane technology. During the next 5–10 years, some mercury cell plants and diaphragm cell plants will be converted to membrane or shut down because of poor production economics or environmental issues. Figure 1 represents the various processes that produce chlorine.

There are some processes that produce only caustic soda and no chlorine, such as the chemical caustic soda process that uses soda ash as the raw material. This process accounts for 1–2% of the total world capacity of caustic soda. Total caustic soda capacity in 2000 was ~56 million dry metric tons. Since there are sources of chlorine that do not produce caustic soda, the production ratio of caustic soda to chlorine in any given year in some countries, such as the United States, is not the theoretical ratio of 1.1. The total nameplate capacity for soda ash in 2000 was ~43 million metric tons and capacity for potassium hydroxide was 1.4 million metric tons (5,6).

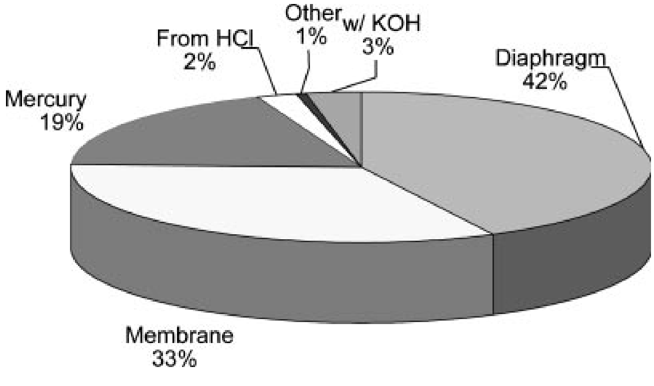


Fig. 1. Technologies for manufacturing chlorine in 2000. Total capacity = 53×10^6 t (5,6).

2. Physical Properties

Table 1 presents characteristic properties of chlorine; further details are available (8–11). References 8 and 10, in particular, contain extensive tabulations of data and graphs of some of the more frequently used properties. Here, the data are described by the following equations: The vapor pressure P (in kPa) can be calculated in the temperature range 172–417 K from the equation 1.

$$\ln P = A - B/T - C\ln T + DT + E(F - T)\ln(F - T)/FT \qquad (1)$$

where $A = 62.402508$, $B = 4343.5240$, $C = 7.8661534$, $D = 0.010666308$, $E = 95.248723$, and $F = 424.90$. The latent heat of vaporization in the range 0 to −80°C, which covers nearly all liquefaction operations is, in kilojoules per kilogram (kJ/kg):

$$\lambda = 268.5140 - 0.63197t - 0.00191245t^2 - 7.7778\text{E}{-}06t^3 \qquad (2)$$

Table 1. **Physical Constants of Chlorine**

Property	Value
CAS Registry number	[7782-50-5]
atomic number	17
atomic weight (carbon-12 scale)	35.453
stable isotope abundance, atom %	
^{35}Cl	75.53
^{37}Cl	24.47
electronic configuration in ground state	[Ne]$3s^23p^5$
melting point, °C	−100.98
boiling point at 101.3 kPa(°C)	−33.97
gas density relative to air	2.48
critical density, kg/m^3	573
critical pressure, kPa	7977
critical volume, m^3/kg	0.001745
critical temperature, °C	143.75
critical compressibility	0.284777
gas density, kg/m^3 at 0°C and 101.3 kPa	3.213
gas viscosity, mPa.s at 20°C	0.0134
liquid viscosity, mPa.s at 20°C	0.346
gas thermal conductivity at 20°C, W/m K	0.00866
liquid thermal conductivity at 20°C, W/m K	0.120
latent heat of vaporization, kJ/kg	287.75
latent heat of fusion, kJ/kg	90.33
heat of dissociation, kJ/mol	2.3944
heat of hydration of Cl$^-$, kJ/mol	405.7
standard electrode potential, V	1.359
electron affinity, eV	3.77
ionization energies, eV	13.01, 23.80, 39.9, 53.3, 67.8, 96.6, and 114.2
specific heat at constant pressure	0.481
specific heat at constant volume	0.357
specific magnetic susceptibility at 20°C, m^3/kg	-7.4×10^{-9}
electrical conductivity of liquid at-70°C, (Ω cm)$^{-1}$	10^{-16}
dielectric constant at 0°C (wavelengths > 10 m)	1.97

The following equations correlate the density, viscosity, and thermal conductivity of saturated liquid (10):

$$\rho = 573 + 1060.6083Y - 160.418Y^2 + 837.08192Y^3 - 247.20716Y^4 \quad (3)$$

$$\ln \mu_l = -2.64947 + 484.686/(T + 12.2345) \quad (4)$$

$$\kappa = 0.2458 - 3.094\text{E}{-04}T - 4.053\text{E}{-07}T^2 \quad (5)$$

where ρ = density, kg/m^3 $Y = (1 - T_r)^{1/3}$

T_r = reduced temperature
μ = viscosity, mPa s (or centipoise)
T = temperature, K
κ = thermal conductivity, W/(m K)
t = temperature, °C

and the transport properties of the gas (at 1atm):

$$C_p = 0.605770219 - 4.6076698\text{E}{-05}T - 41.8722507/T + 2408.76803/T^2 \quad (6)$$

$$\ln \mu_g = -2.40317 - 1117.9/(T + 292.683) \quad (7)$$

$$\ln \kappa = -2.7230 - 1004.4/(T + 202.68) \quad (8)$$

where C_p = heat capacity, kJ/kg K

Chlorine is somewhat soluble in water and in salt solutions, its solubility decreasing with increasing temperature or salt strength. It is partially hydrolyzed in aqueous solution according to equation 9.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (9)$$

This hydrolysis increases the solubility by reducing the partial pressure corresponding to a given amount of dissolved chlorine. Taking the equilibrium of reaction 9 into account, chlorine's solubility in water at a given temperature can be expressed as a function of its partial pressure by

$$S = \text{HP} + (K\text{HP})^{1/3} \quad (10)$$

where
H = Henry's law solubility constant for molecular chlorine
K = equilibrium constant for reaction 9.

Chlorine forms a hydrate, containing 7–8 molecules of water per molecule of chlorine below 9.6°C at atmospheric pressure. These crystals are greenish-yellow in color. Chlorine hydrate forms greenish-yellow crystals below 9.6°C at atmospheric pressure. It does not exist above the quadruple point temperature of 28.7°C. It has a density of ~1.23 and therefore floats on liquid chlorine when deposited in a liquefaction system. Table 2 gives data for the solubility of chlorine in solvents other than water.

Table 2. **Solubility of Chlorine in Various Solvents**[a]

Solvent	Temperature, °C	Solubility
sulfuryl chloride	0	12.0
disulfur chloride	0	58.5
phosphoryl chloride	0	19.0
silicon tetrachloride	0	15.6
titanium tetrachloride	0	11.5
dimethylformamide	0	123[b]
acetic acid (99.84%)	0	11.6[b]
benzene	10	24.7
chloroform	10	20.0
carbon tetrachloride	20	17[c]
hexachlorobutadiene	20	22[c]

[a] Solubility in wt % unless otherwise noted.
[b] g/100 mL.
[c] mol%.

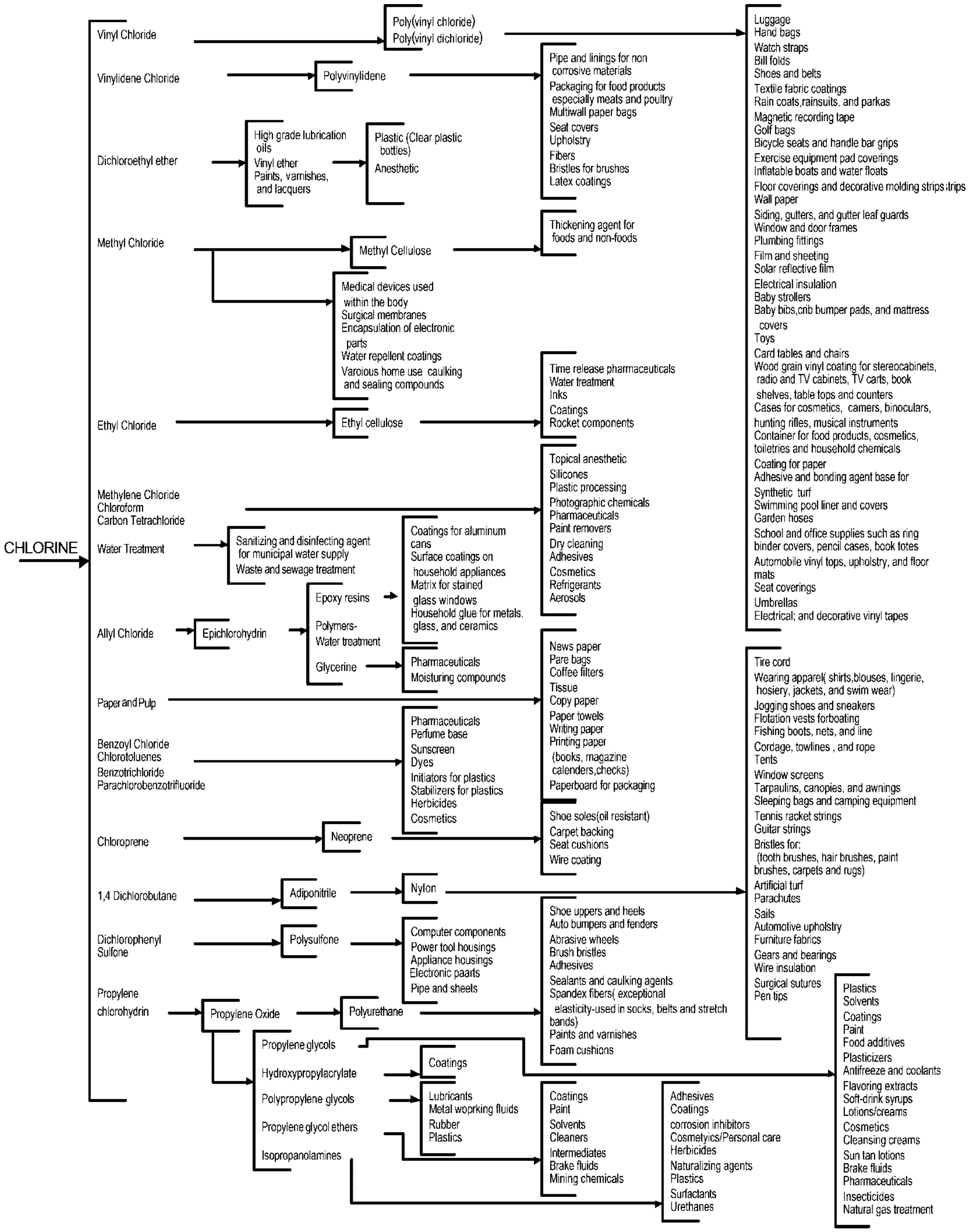
3. Chemical Properties

Martin and Longpre (9) discuss the chemical properties of chlorine. Chlorine usually exhibits a valence -1 in compounds, but it also exists in the formal positive valence states of + 1 ($NaClO$ [7681-52-9]), +3 ($NaClO_2$ [7758-19-2]), +5 ($NaClO_3$ [7775-09-9]), and +7 ($NaClO_4$ [7601-89-0]).

Molecular chlorine is a strong oxidant and a chlorinating agent, adding to double bonds in aliphatic compounds or undergoing substitution reactions with both aliphatics and aromatics. Tables 3 and 4 present significant industrial reaction products of chlorine and hydrochloric acid (12). Chlorine is very reactive under specific conditions but is not flammable or explosive. Reactions with most elements are facile, but those with nitrogen, oxygen, and carbon are indirect. Chlorine reacts with ammonia to form the explosive compound NCl_3. It does not react with hydrogen at normal temperatures in the absence of light. However, at temperatures 250°C, or in the presence of sunlight or artificial light of ~470-nm wavelength, H_2 and Cl_2 combine explosively to form HCl. Explosive limits of mixtures of pure gases are ~8% H_2 and ~12% Cl_2 (v/v) (see Fig. 2). These limits depend on temperature and pressure, and they can be altered by adding inert gases such as nitrogen and carbon dioxide. Most plants control the process to keep the hydrogen concentration below 4%.

Dry chlorine reacts combustively with most metals at sufficiently elevated temperatures. Aluminum, arsenic, gold, mercury, selenium, tellurium, and tin react with dry chlorine in gaseous or liquid form at ordinary temperatures; carbon steel ignites at ~250°C, depending on physical shape; and titanium reacts violently with dry chlorine. Wet chlorine is very reactive and very corrosive because of the formation of hydrochloric and hypochlorous acids (see eq. 9). Metals stable to wet chlorine include platinum, silver, tantalum, and titanium. The apparent anomaly in the behavior of titanium, which is stable in wet chlorine but explosive with dry chlorine, is due to the formation of a protective layer of

Table 3. **End Uses of Chlorine**[a]



---

[a] (With permission from SRI International)

Table 3 *(Continued)*

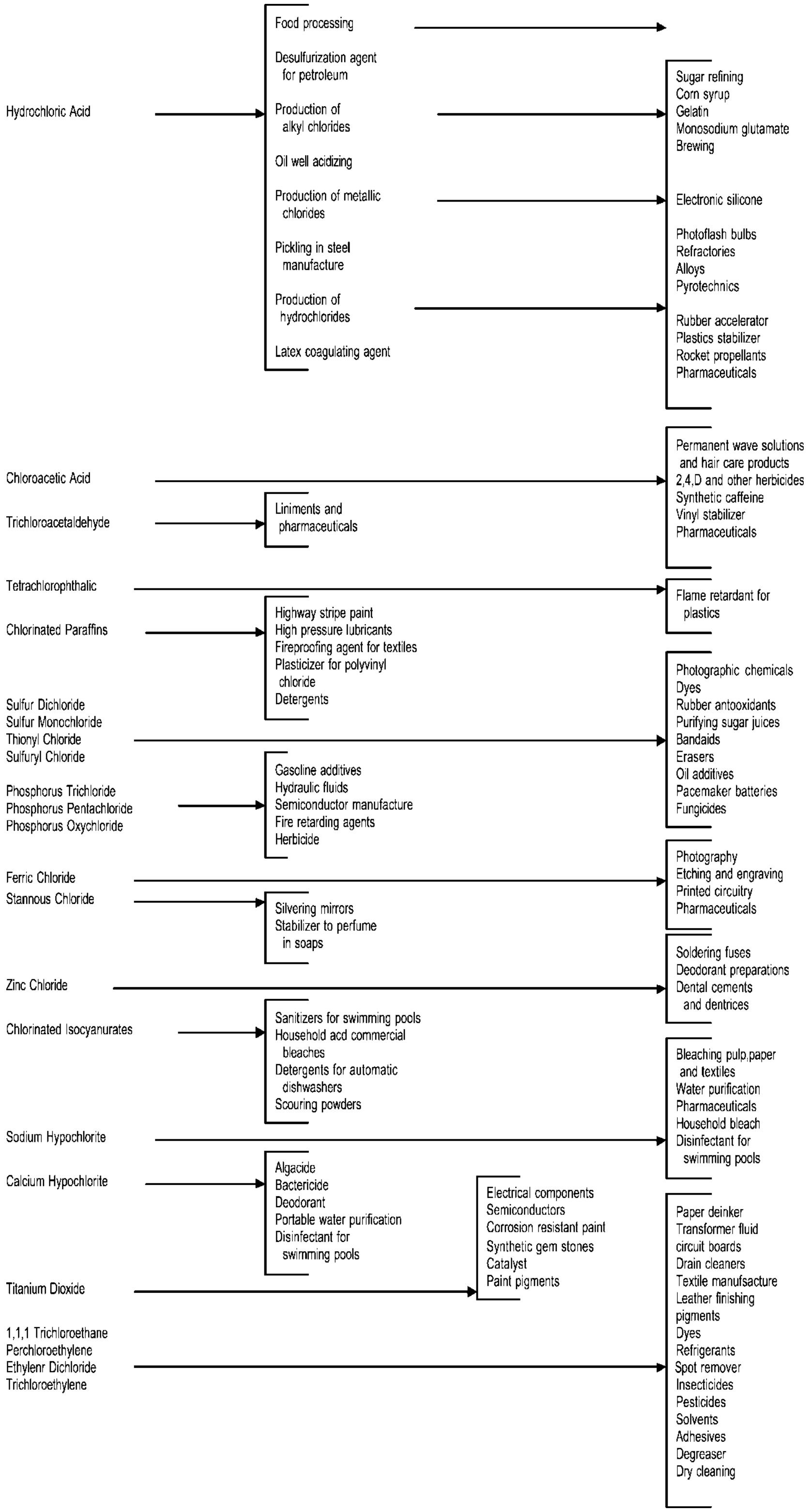


Table 4. **Operating Characteristics of ELTECH Diaphragm Cells**

Parameter	MDC 29		MDC 55		H2A		H4	
operating range, kA	40	80	75	150	50	80	90	150
chlorine capacity, t/day[a]	1.21	2.43	2.26	4.55	1.51	2.42	2.71	4.54
caustic capacity, t/day	1.36	2.74	2.55	5.14	1.70	2.73	3.06	5.13
hydrogen capacity, m^3/day	399	798	748	1497	498	798	897	1496
current density, kA/m^2	1.38	2.76	1.37	2.74	1.38	2.21	1.40	2.33
cell voltage, V (includes intercell bus)	2.97	3.60	2.97	3.59	2.97	3.35	2.98	3.40
energy consumption, dc kWh/t of Cl_2	2363	2847	2363	2839	2363	2655	2371	2694
modified diaphragm life, days	425	200	410	200	410	300	425	375
anode life, year	10–15	8–10	10–15	8–10	10–15	8–10	10–15	8–10
cathode life, year	10–15	5–8	10–15	5–8	10–15	5–8	10–15	5–8
distance between cells[b], m	1.6		2.13		2.32		3.05	

[a] To convert to short ton, multiply by 1.1.

[b] distance from center to center and side by side positioning with bus connected.

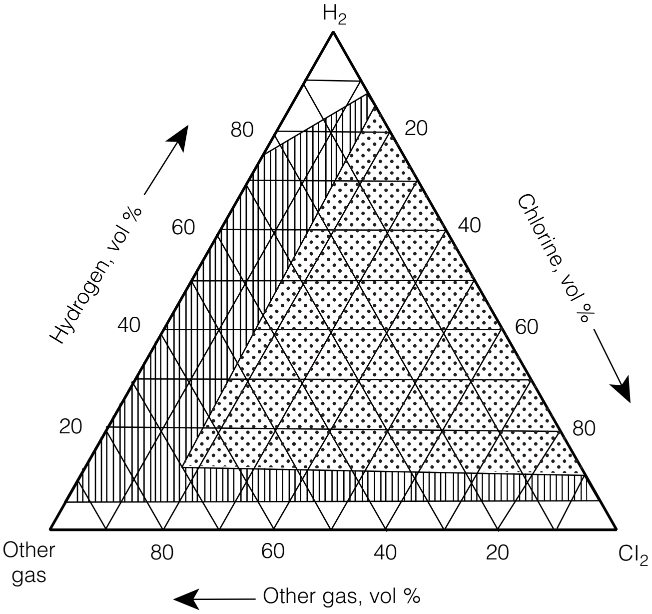


Fig. 2. Explosive limits of Cl_2–H_2–other gas mixtures where the area with vertical lines represents the explosive region in the presence of residual gas from chlorine liquefaction (O_2, N_2, CO_2) and the area with black dots refers to the presence of inert gases (N_2, CO_2).

TiO_2 when the partial pressure of water vapor is sufficiently high. Tantalum is the most stable metal to both dry and wet forms.

Chlorine reacts with alkali and alkaline earth metal hydroxides to form bleaching agents such as NaOCl:

$$Cl_2 + 2\,NaOH \rightarrow NaCl + NaOCl + H_2O \tag{11}$$

Reaction of hypochlorite with ammonia produces hydrazine:

$$2\,NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + H_2O \tag{12}$$

TiO_2 reacts with chlorine in the presence of carbon in the manufacture of $TiCl_4$, an intermediate in the production of titanium metal and pure TiO_2 pigment:

$$TiO_2 + 2Cl_2 + C(\text{or } 2C) \rightarrow TiCl_4 + CO_2(\text{or } 2CO) \tag{13}$$

$SiCl_4$ is produced by a similar reaction with SiO_2.

Chlorine reacts with saturated hydrocarbons and certain of their derivatives by substitution of hydrogen to form chlorinated hydrocarbons and HCl. Thus, methanol and methane chlorinate to form methyl chloride, which can continue to react with chlorine to form methylene chloride, chloroform, and carbon tetrachloride. Reaction of chlorine with unsaturated hydrocarbons results in saturation of the double or triple bond. This is a very important reaction in the production of ethylene dichloride, an intermediate in the manufacture of vinyl chloride and the largest consumer of chlorine:

$$CH_2{=\!=}CH_2 + Cl_2 \rightarrow CH_2Cl{-\!-}CH_2Cl \tag{14}$$

Organic substitution chlorinations utilize only one-half of the chlorine they consume; the other one-half is converted to HCl. While addition chlorinations consume the whole chlorine molecule, the resulting product may be dehydrochlorinated, again releasing one-half the chlorine value as HCl. This is the basis of manufacture of vinyl chloride monomer:

$$CH_2Cl{-\!-}CH_2Cl \rightarrow CH_2{=\!=}CHCl + HCl \tag{15}$$

The amount of HCl that results from these reactions would far exceed the market demand. This situation is relieved by the use of oxychlorination, in which oxygen is mixed with the feedstock and has the effect of converting the HCl byproduct back to chlorine. Oxychlorination is the favored process for ethylene dichloride:

$$CH_2{=\!=}CH_2 + 2\,HCl + \tfrac{1}{2}O_2 \rightarrow CH_2Cl{-\!-}CH_2Cl + H_2O \tag{16}$$

This allows the use of by-product HCl in the process. Alternatively, vinyl chloride manufacture can be by balanced oxychlorination, using the proper amount of fresh chlorine along with the HCl produced in reaction 15.

Direct chlorination of vinyl chloride generates 1,1,2-trichloroethane [79-00-5], from which vinylidene chloride is produced. Hydrochlorination of vinylidene chloride produces 1,1,1-trichloroethane [71-55-6]. This was a commercially important solvent whose use is being phased out under the terms of the Montreal Protocol. Tri- and tetrachloroethylene are manufactured by chlorination, hydrochlorination, or oxychlorination reactions involving ethylene. Aromatic solvents or pesticides such as mono-, di-, and hexachlorobenzene are produced by reaction of chlorine with benzene. Monochlorobenzene is an intermediate in the manufacture of phenol, aniline, and dyes (see CHLOROCARBONS AND CHLOROHYDROCARBONS, TOXIC AROMATICS).

4. Manufacture and Processing

4.1. Historical. In 1774, Swedish apothecary Carl W. Scheele first generated and collected chlorine by reacting manganese dioxide and hydrochloric acid. Scheele also discovered chlorine's bleaching action, after placing some leaves and flowers in a bottle containing the gas. Textile manufacturers in France produced the first commercial liquid chlorine bleach (13), by bubbling chlorine through a potash solution, in 1789.

Salt was first electrochemically decomposed by Cruickshank in 1800, and in 1808 Davy confirmed chlorine to be an element. In the 1830s, Michael Faraday, Davy's laboratory assistant, produced definitive work on both the electrolytic generation of chlorine and its ease of liquefaction. In 1851, Watt obtained the first English patent for an electrolytic chlorine production cell (14).

Through the 1880s and 1890s, producers in England, Canada, and the United States refined chlorine technology: Siemens developed electric generators; the Griesheim Company (Germany) invented the first practical diaphragm cell; Castner produced the first commercially viable mercury cell; and German producers found that water-free chlorine could be safely shipped in ordinary iron or steel pressure vessels. Thus by the early 1900s, chlorine was produced in mercury and diaphragm electrolytic cells and routinely shipped in liquid form. In 1913, Altoona, Pennsylvania became the first of many cities to treat sewage with liquid chlorine. Throughout the early and mid-1900s a wide variety of other chlorine uses were discovered. Presently, chlorine ranks in the top 10 volume chemicals produced in the United States.

Early demand for chlorine centered on textile bleaching, and chlorine generated through the electrolytic decomposition of salt sufficed. Sodium hydroxide was produced by the lime-soda reaction, using sodium carbonate readily available from the Solvay process. Increased demand for chlorine for polyvinyl chloride (PVC) manufacture led to the production of chlorine and sodium hydroxide as coproducts. Solution mining of salt and the availability of asbestos resulted in the dominance of the diaphragm process in North America, whereas solid salt and mercury availability led to the dominance of the mercury process in Europe. Japan imported its salt in solid form and, until the development of the diaphragm and then the membrane process, also favored the mercury cell for production.

4.2. Anodes. Graphite was exclusively used as the anode for chlorine production for >60 years even though it exhibited high chlorine overpotential and dimensional instability caused by the electrochemical oxidation of carbon to CO_2, which led to an increased electrolyte ohmic drop, and hence to high energy consumption during use. In the late 1960s, H.B. Beer's (15) invention of noble metal oxide coatings on titanium substrates as anodes revolutionized the chlor-alkali industry. The most widely used anodes were ruthenium oxide and titanium oxidez-coated titanium, which operated at low chlorine overpotential with excellent dimensional stability. Escalating power costs, triggered by the oil crisis in the mid-1970s, accelerated the transition of the chlor-alkali industry from graphite to metal anodes. Presently, $RuO_2 + TiO_2$ coated titanium anodes are exclusively used as the anodes. These anodes are supplied in the United States only by deNora, Electrode Products Inc. and ELTECH Systems Corporation under the trade name DSA, for dimensionally stable anodes.

The DSA electrode is a titanium substrate coated with titanium and ruthenium oxide mixture containing >30 mol% precious metal oxide, the precious metal loading ranging from 5 to 20 g/m^2. These coatings are formed on titanium mesh substrates by thermal decomposition. Ruthenium and titanium salts dissolved in organic solvent (eg, butanol), are applied to the Ti mesh and fired at 500°C in air to obtain the mixed oxides.

Both RuO_2/TiO_2 based coatings are polycrystalline and structurally complex. The oxides exist in the catalytic layer as $Ti_{(1\text{-}n)}Ru_nO_2$, where $n < 1$. The coatings exhibit a "mud-cracked" surface area of 200–500 cm^2 per apparent cm^2, the exact value being a function of the heat treatment and the coating composition. Two coatings that predominate in the industry are the original Beer coating containing a Ti/Ru mole ratio of 2:1 and a three-component coating with a mole ratio of 3Ru/2Sn/11Ti. This coating has a $RuO_2 + SnO_2$ loading of 1.6 mg/cm^2. It generates 22–25% less oxygen than RuO_2/TiO_2 coatings.

The Ru—Ti and Ru—Sn—Ti based compositions were prone to degradation via Ru losses in membrane cell operations, thereby limiting their life to 2–3 years. This problem was overcome with Ru–Ir–Ti coatings with total precious metal loading of 10–12 g/m^2 and Ru/Ir ratio of 1:1 based on mol% or wt%. These coatings are claimed to last >5 years in membrane cell operations (16,17). References (18) and (19) give more details on the various patented compositions and methods of preparation.

DSA anodes exhibit long life, very low operating voltage, and high chlorine efficiency. They are tolerant to a wide range of operating conditions, although performance degradation can occur when the percentage of oxygen generated is high. Harmful conditions include operation at feed brine pH values of >11 and at feed brine NaCl concentrations of <280 g/L. Exposure to caustic or fluorides results in the dissolution of RuO_2 as ruthenate ion or as ruthenium fluoride, and titanium as soluble titanium fluoride. Deposition of foreign matter such as MnO_2 or $BaSO_4$ can result in blockage of active sites on the surface and lead to the failure of the catalytic coatings, as revealed by the increased anode potential during service.

The mechanism of coating failure appears to depend on the type of cell in which the anode is operated. Life in diaphragm cells is at least 12 years; in mercury cells, it is considerably shorter, ~3–4 years. The unavoidable occurrence of minor short circuits, through contact with the mercury cathode, causes gradual physical wear of the anode coating. The limiting factor in membrane and diaphragm cells, in the absence of impurity-related effects, is the loss of RuO_2 by dissolution that accompanies high oxygen production and cell shutdowns

(20,21). A reduction in precious metal loading to $<2\ \text{g/m}^2$ or a reduction in ruthenium content to <20 mol% leads to increased anode potentials. When the RuO_2 is lost from the surface layers, it is possible to reactivate the coating (22,23). When the total loading becomes too low, it is necessary to recoat the titanium substrate. Another explanation for the enhanced anode potentials is the formation (and build up) of insulating TiO_2 layer(s) between the coating and the substrate, which lacks direct evidence.

The anode suppliers recommend a feed brine concentration of 300 g/L and $pH < 12$, along with the following maximum limits of impurities (noted in parentheses), in ionic form: Hg (40 ppb); Mn (0.01 ppm); heavy metals (0.3 ppm); total organic content (1 ppm); F^- (1 ppm); Ba (0.4 ppm).

4.3. Electrolytic Cell Operating Characteristics. Diaphragm cell technology is the source for generating the largest volume of chlorine, followed by the membrane cell process, and then the mercury process. However, the membrane process will dominate in the future, reflecting its ecological and economical benefits associated with it versus the other technologies. Over the past 10 years, neither new diaphragm nor mercury plants have been built. The electrolytic designs that are currently licensed or used are discussed have with a special emphasis on the membrane cells.

Depending on operating parameters (ie, current density, cell voltage, and current efficiency), the electrical energy consumption in membrane chlor-alkali electrolysis is between 1950 and 2300 kWh/t of chlorine. The amount of energy required to concentrate caustic soda from 32 to 50 wt% varies between 700 and 800 kWh/t (basis: medium pressure steam) of chlorine for a double-effect evaporator. Energy savings may justify investment in a third effect.

The electrical energy consumption in diaphragm chlor-alkali electrolysis is ~10–20% higher than in membrane technology. In addition, diaphragm cells operate at a low caustic soda concentration of ~11wt%, and hence the energy requirements to achieve the commercial concentration of 50% wt of caustic soda are much higher compared to the membrane process. The overall plant efficiency, defined as the ratio of the heat of the reaction to the sum of the endothermic processes and the electrical energy in to the cell, with diaphragm chlor-alkali cells is ~23%, while the corresponding value for membrane cells is ~35–40%.

4.4. Cell Technologies. As stated earlier, there are three primary electrolytic technologies based on mercury, diaphragm and membrane cells, that are used to produce chlorine and caustic. The currently available membrane cell technologies, with a brief description of the mercury and diaphragm cell technologies, are presented below.

Mercury Cells. Although no mercury cell plants were built over the past 15–20 years, ~20% of the world's chlorine (and <6% of the chlorine in the United States) is produced using the mercury cell technology of Uhde, DeNora, Olin, Solvay, Krebs, and others. The mercury cell process (Fig. 3) consists of two electrochemical cells: the electrolyzer and the amalgam decomposer.

The mercury cell has a steel bottom with rubber coated steel sides, as well as end boxes for the brine and mercury feed and exit streams with a rubber or rubber-lined steel covers. Adjustable metal anodes hang from the top and mercury flows on the inclined bottom. The current flows from the steel bottom to the flowing mercury. Sodium chloride brine of 25.5% salt strength, fed from

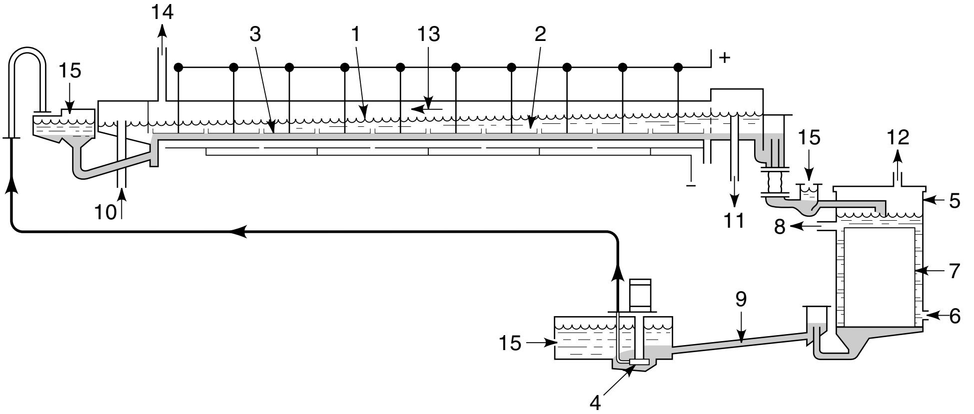


Fig. 3. Mercury cathode electrolyzer and decomposer : (*1*) brine level; (*2*) metal anodes; (*3*) mercury cathode flowing along base plate; (*4*) mercury pump; (*5*) vertical decomposer; (*6*) water feed to the decomposer; (*7*) graphite packing promoting the decomposition of the amalgam; (*8*) caustic liquor outlet; (*9*) denuded mercury; (*10*) brine feed; (*11*) brine exit; (*12*) hydrogen exit from the decomposer; (*13*) chlorine gas space; (*14*) chlorine exit; (*15*) wash water. Courtesy of Chlorine Institute Inc.

the inlet end box, is electrolyzed at the anode to produce chlorine gas, which leaves from the top of the cell. The sodium ions get discharged at the cathode to form sodium amalgam containing 0.25–0.4% Na, which flows out of the outlet end box. The sodium amalgam is subsequently reacted with water in the decomposer, packed with graphite particles, to form 50% NaOH and H_2. The unreacted brine out of the exit end box is resaturated and recycled back to the cells along with the denuded mercury from the decomposer.

Mercury cells operate efficiently because the hydrogen overpotential is high on mercury, favoring the sodium amalgam formation over the hydrogen evolution reaction. However, the brine should be free of impurities such as vanadium or chromium that will lower the hydrogen overvoltage, allowing hydrogen to form in dangerous quantities.

Developments in mercury cell operations over the past 10–15 years have been aimed toward lowering the energy consumption of the cells and minimizing the mercury losses to the air, water, or the products of electrolysis and the decomposer. Most plants operating with the mercury cells have complied with and sometimes surpassed the standards set by the local government and the federal agencies. The Environmental Protection Agency's (EPAs) National Emission Standards for Hazardous Air Pollutants for mercury currently call for a maximum mercury level of 1000 g in air at point source and 1300 g/day as fugitives. These standards are expected to be revised in the year 2002. References (24) and (25) give additional details related to the mercury cell technologies.

Diaphragm Cells. The first chlorine cell incorporating a percolating asbestos diaphragm was designed by E. A. LeSueur in the 1890s. In this cell, brine flowed continuously into the anolyte and subsequently through a diaphragm into the catholyte. The diaphragm separates the chlorine liberated at the anode from the sodium hydroxide and hydrogen produced at the cathode.

Failure to separate the chlorine and sodium hydroxide leads to the production of [sodium hypochlorite [7681-52-9], NaOCl, which undergoes further reaction to sodium chlorate [7775-09-9], $NaClO_3$. The commercial process to produce sodium chlorate is, in fact, by electrolysis of brine in a cell without a separator (see CHLORINE OXYGEN ACIDS, SALTS).

The early cells incorporated a horizontal asbestos sheet as the diaphragm. During the 1920s, this type of cell was the most widely used in the world and a few are still in operation. Subsequently, three basic types of diaphragm cells have been developed: rectangular vertical electrode monopolar cells, cylindrical vertical electrode monopolar cells, and vertical electrode filter press bipolar cells.

Asbestos Diaphragms. The earliest diaphragms were made of asbestos paper sheets. Asbestos was selected because of its chemical and physical stability and because it is a relatively inexpensive and abundant raw material. The vacuum-deposited asbestos diaphragm, developed in the 1920s, was the diaphragm of choice until 1971, when it was supplanted by the Modified Diaphragm (trademark of ELTECH Systems, Inc.) (26). In its most common form, the Modified Diaphragm contains fibrous polytetrafluoroethylene (PTFE) and a minimum of 75% asbestos. The polymer, following fusion, stabilizes the asbestos, lowers cell voltage, and allows the use of the expandable DSA anode (27), which further lowers the cell voltage (28). The Modified Diaphragm in various formulations is the most common diaphragm in use today.

The toxicological problems associated with asbestos have been widely publicized and an EPA ban was overturned in 1991. Asbestos bans affecting the chlor-alkali industry exist in France, Argentina, and Scandinavia and indirectly in Brazil.

Non-Asbestos Diaphragms. Numerous patents relating to non-asbestos diaphragms have been issued, and three have demonstrated commercial success sufficient to warrant the conversion of one or more cell rooms.

Polyramix fiber is a zirconia-PTFE deposited separator (29) developed by ELTECH Systems in use in five cell rooms commercially. Three of these cell rooms have been converted to Polyramix diaphragms, while two others are being converted. Polyramix separators offer longer diaphragm life, lower energy consumption, and can be reclaimed, or cleaned, with inhibited HCl to restore performance.

PPG Industries has also developed a non-asbestos diaphragm referred to as the Tephram diaphragm (30). This technology uses vacuum depositing to produce a base diaphragm composed of PTFE fluoropolymer materials and inorganic particulate materials. This diaphragm has also exhibited greatly extended life in comparison to asbestos and equal or better voltage and current efficiency characteristics. PPG uses the Tephram diaphragm in a significant portion of its Chlor/Alkali operations.

Chlor-Alp has developed a synthetic two layer separator consisting of an activated nickel deposited sublayer with a synthetic separator deposited on top; their two cell rooms in France are being converted to that technology (31).

Electrolyzers. Various designs of bipolar and monopolar diaphragm electrolyzers were developed and used in commercial operations (32). These include the bipolar cells of Dow and the Glanor cells of PPG, and the monopolar cells of the Eltech/Uhde HU-type, which have not been licensed for use during the

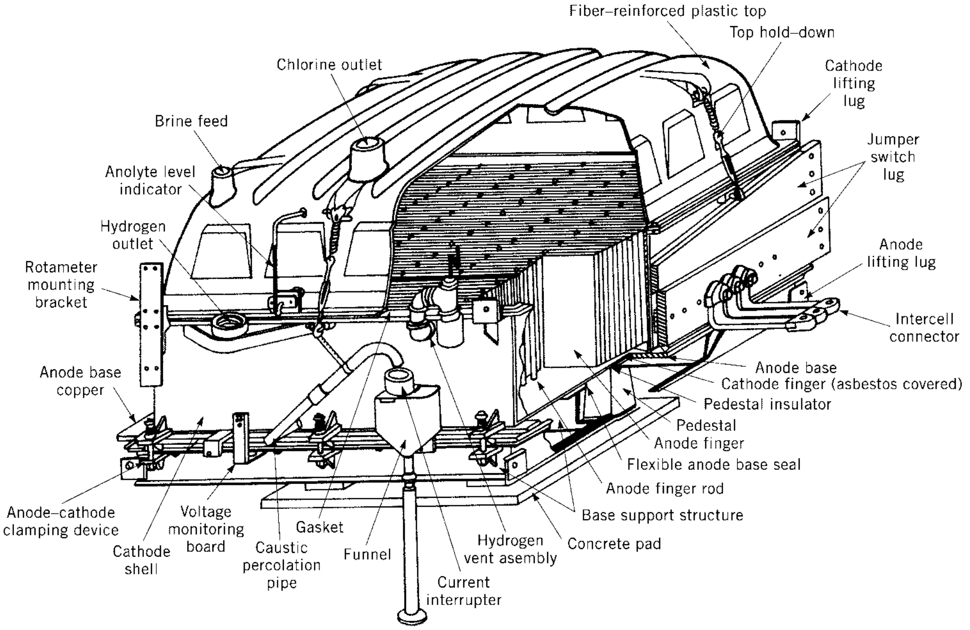


Fig. 4. Cut view of ELTECH H-4 diaphragm cell operating at a nominal rating of 150 kA.

past 15 years. The sole supplier of diaphragm cell technology, at present, is ELTECH Systems, Inc., located in Chardon, Ohio.

ELTECH Monopolar Electrolyzers. ELTECH supplies monopolar diaphragm electrolyzers of two designs: the ELTECH H-type (33,34) shown in Figure 4 and the MDC-type (34,35) in Figure 5.

The H-series of monopolar cells incorporate DSA anodes and operate at high current densities. The H-series employs cathode tubes having both ends open and extending across the cell, similar to the MDC cells. ELTECH has introduced a series of improvements to the design and performance of its monopolar diaphragm cells. The MDC series cathodes have been redesigned to replace the tube sheets and horizontal strap supports with copper corrugations that extend and are welded to the current carrying side plate to which the intercell connectors are bolted. Similar construction, which also features explosion bonded side plates, is offered for the H-series cathodes. The cathodes are also designed so that they can be stress relieved, which, along with the copper internals, extends the life of the cathode by at least 25%. These new cathodes are called ATC for advanced technology cathode. The conventional MDC cathode construction featuring tubes welded through a pair of tube sheets is being phased out.

New anode designs offer lower resistance, and can be operated at zero gap with Polyramix diaphragms (29,30). The low voltage anode (LVA) features a solid conductor bar and 1-mm thick expanders to reduce structure drop. The energy saving anode ESA features expanded mesh with micromesh continuously welded to the substrate, in addition to the LVA improvements, and is designed to operate at zero gap with the Polyramix diaphragm.

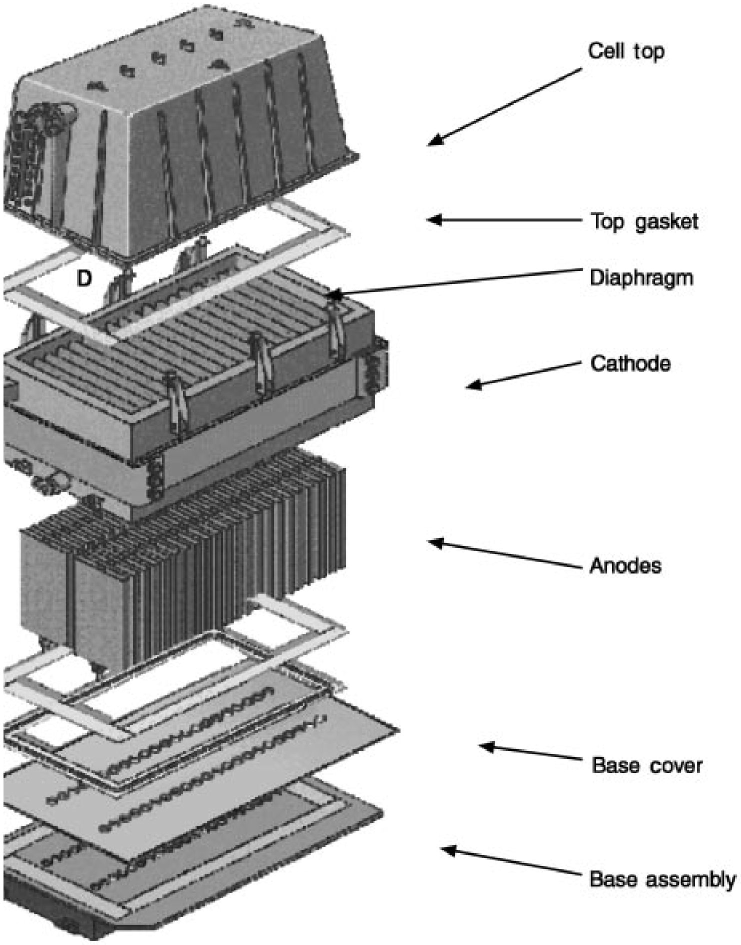


Fig. 5. Exploded view of an ELTECH MDC-55 cell.

The most effective improvements, however, involve rebuilding the cell to increase the electrode areas by reducing the cathode tube thickness and the spacing between the electrodes. Cell areas have been increased from 14–24%, depending on design.

The life of a Polyramix (PMX) diaphragm is several times that of a polymer modified asbestos (PMA) diaphragm. Furthermore, *in situ* diaphragm reclamation procedures have been developed that permit the life of the PMX diaphragm to be extended to match the life of the cathode internals. Titanium base covers (TIBAC), are replacing rubber covers to protect the base. Improved gaskets have been developed to extend the life of the modern diaphragm cell assembly to 5 years or more. Advanced diaphragm cell technology (ADCT), incorporating these improved cell components is claimed to offer electrical energy reduction of 10–15% over conventional diaphragm cell technology using expandable anodes and polymer modified asbestos diaphragms.

Table 5. **Characteristic Features of Current Membrane Technologies**

Supplier	Effective membrane area (m^2)	Max. number of cells per electrolyzer	Circuit load (kA)	Current density (kA/m^2)	Specific energy consumption (kWh/t NaOH, 100%)
Bipolar electrolyzers					
Asahi Kasei, ML 32 or ML 60	2.72 or 5.05	150	5.4–30.3	2–6	2100 (at 4 kA/m^2)
CEC, BiTAC-800	3.28	80	5–19.65	1.5–6	2150 (at 5 kA/m^2)
ELTECH, ExL^B	1.5	60	2.25–10.5	1.5–7	2100 (at 5 kA/m^2)
Krupp Uhde/Uhde Nora, BL-2.7	2.7	160	5.4–16.3	2–6	2130 (at 5 kA/m^2)
Ineos Chlor Ltd	2.89	160	5.79	6	2190 (AT 6 kA/m^2)
Monopolar electrolyzers					
CEC, DCM 416 × 2	3.03	32	194	4	2250 (at 4 kA/m^2
ELTECH, ExL^{Ma}	1.5	30	15–180	1.5–6	2150 (at 5 kA/m^2)
Ineos, FM-21-SP or FM-1500	2 × 0.21	60 or 120	30–480	1.5–4	2140 (at 4 kA/m^2)

[a] Based on the ELTECH MGC-Electrolyzer.

Over 20,000 t/day of chlorine capacity has been licensed with MDC cells. Table 5 lists the operating characteristics of the four most common ELTECH diaphragm cells.

Ion-Exchange Membrane Cells. As stated earlier, the membrane chlor-alkali electrolysis is the state-of-the-art process and is the choice of cell technology for grass root plants and for expansion/conversion projects. The conversion of a mercury or a diaphragm plant to membrane cell operations often is an interesting alternative to building a new plant, as investment costs can be reduced by integrating the membrane electrolyzers into the existing infrastructure.

The key component of a membrane cell is the ion exchange membrane, which should be chemically stable, withstanding the extremely aggressive conditions in an electrolysis cell (ie, chlorine in the anolyte and concentrated caustic in the catholyte) and offering excellent ion-exchange selectivity to meet the electrochemical requirements. The first membrane of such a type was developed by DuPont in the early 1970s (37). Membrane-cell technology was first developed, demonstrated, and commercialized in Japan. In 1978, the first bilayer membrane exhibiting low electrical resistance and high current efficiency was introduced.

In the year 2000, ~33% of the world chlorine production was met by membrane cell technology, and this percentage will continue to grow.

Principles. In a membrane cell, a cation-exchange membrane separates the anolyte and the catholyte, as shown in Figure 6. Ultrapure brine (containing <20 ppb of Ca^{2+} and Mg^{2+} ions combined) with a salt content of ~310 g/L NaCl is fed into the anolyte compartment, where chlorine gas is generated at the anode. The sodium ions, together with the associated water molecules, migrate through the membrane into the catholyte. The membrane effectively prevents the migration of hydroxyl ions into the anolyte. Unlike the separators used in

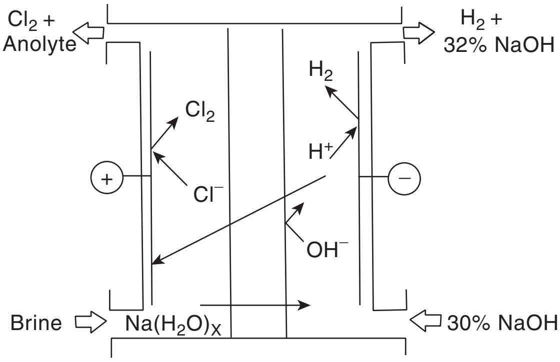


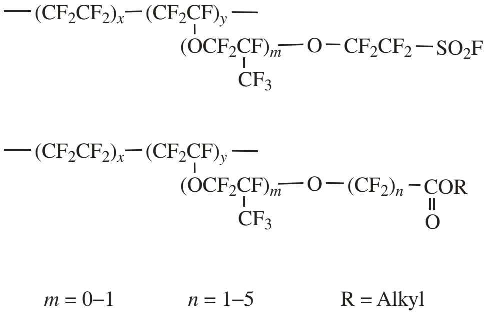
Fig. 6. Principle of the membrane cell.

the diaphragm-cell process, the cation-exchange membrane mostly prevents the migration of chloride ions into the catholyte. The depleted brine from the anode compartment is resaturated with salt to maintain the required salt concentration and fed back to the cells. On the catholyte side, water is electrolyzed at the cathode to form hydrogen and hydroxyl ions, which combine with the sodium ions transported from the anolyte to form caustic soda. Present-day membranes perform optimally at a caustic concentration of ~32–35%. The product caustic concentration is adjusted by adding demineralized water to the recirculating caustic.

Membranes. The membrane is the most critical component of the membrane-cell technology. It determines the current efficiency, cell voltage, and hence the energy consumption for the production of chlorine and caustic. An ideal ion-exchange membrane should exhibit:

- High selectivity for the transport of sodium or potassium ions,
- Negligible transport of chloride, hypochlorite, and chlorate ions,
- Zero back-migration of hydroxide ions,
- Low electrical resistance,
- Good mechanical strength and properties with long term stability (38).

An ion-exchange membrane exhibiting these characteristics was first developed by DuPont, based on perfluorosulfonate polymers (39–46). These membranes achieved high efficiency and low voltage only at low caustic concentrations (~10–12%). At high caustic strengths, there was significant back-migration of caustic into the anode compartment, which resulted in low caustic and chlorine current efficiencies (47,48). Next, Asahi Glass Company of Japan developed a cation exchange membrane, based on perfluorocarboxylic acid polymer. This showed high caustic efficiencies at high caustic concentrations but exhibited high electrical resistance due to the low water content in the membrane (49). The membrane manufacturers then combined the best features of the perfluorosulfonic acid and perfluorocarboxylic acid polymers (Fig. 7) to develop composite membranes with sulfonic acid layers facing the anolyte side and carboxylic acid layers facing the catholyte side, with an intermediate reinfor-



$$\begin{array}{l} -(\mathrm{CF_2CF_2})_x-(\mathrm{CF_2}\underset{|}{\mathrm{C}}\mathrm{F})_y- \\ \qquad\qquad\qquad (\mathrm{OCF_2}\underset{\underset{\displaystyle\mathrm{CF_3}}{|}}{\mathrm{C}}\mathrm{F})_m-\mathrm{O}-\mathrm{CF_2CF_2}-\mathrm{SO_2F} \end{array}$$

$$\begin{array}{l} -(\mathrm{CF_2CF_2})_x-(\mathrm{CF_2}\underset{|}{\mathrm{C}}\mathrm{F})_y- \\ \qquad\qquad\qquad (\mathrm{OCF_2}\underset{\underset{\displaystyle\mathrm{CF_3}}{|}}{\mathrm{C}}\mathrm{F})_m-\mathrm{O}-(\mathrm{CF_2})_n-\underset{\underset{\displaystyle\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OR} \end{array}$$

$m = 0–1 \qquad n = 1–5 \qquad \mathrm{R} = \mathrm{Alkyl}$

Fig. 7. Structural formulas for perfluorosufonate (top) and perfluorocarboxylate groups (bottom) (57).

cing fabric between them (Fig. 8). It is these composite membranes that are currently used in the membrane cells to achieve high current efficiency and low cell voltage at current densities >5 kA/m^2. These composite membranes are prepared by lamination of the perfluorocarboxylate and perfluorosulfonate films, by the chemical conversion of the perfluorosulfonic acid to realize a carboxylate layer thickness of 5–10 μm, or by coextension of the two different polymer films, which will provide high efficiency with low voltage penalty.

An important characteristic of the persulfonate membranes is their ability to achieve the desired transport of sodium ions while hindering the migration of the hydroxyl ions (38). Several theoretical descriptions have been proposed to understand the unique transport character of ions and water molecules across these polymeric membranes. Of these the most popular one is the cluster-network model proposed by Gierke based on experimental evidence supporting the model. According to this description, the ions and the sorbed solutions are in clusters as shown in Figure 9. In a 1200-equivalent weight polymer, the clusters are of 3–5 nm in diameter, each containing ∼70 ion-exchange sites and 1000 water molecules (50,51).

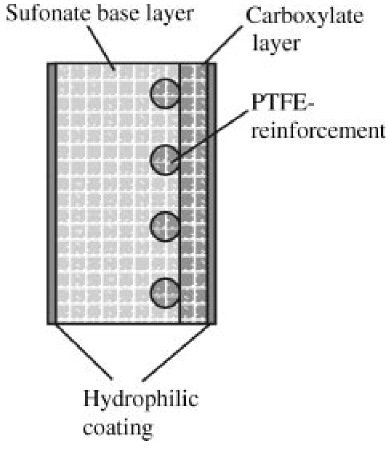


Fig. 8. Structure of a high performance chlor-alkali membrane.

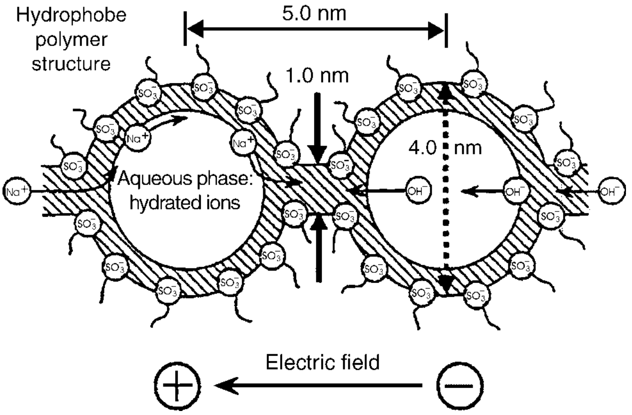


Fig. 9. Principle of the cluster-network model (51).

The counterion, the fixed sites and the swelling water phase are separated from the perfluorocarbon matrix into spherical domains connected by short narrow channels. The fixed sites are embedded in the water phase near the water–fluorocarbon interface. The diameter of these channels is 1 nm. High caustic efficiency, according to this model, is a result of the repulsive electrostatic interaction between the hydroxyl ion and the fixed charges on the surface of the clusters. Hence, the migration of the hydroxyl ion is difficult as it has to overcome a large electrostatic barrier in the channel. This results in high caustic efficiencies. Sodium ion, on the other hand, moves easily from one site to the other because of the favorable potential gradient and the small distances between sites.

A phenomenon of importance during electrolysis is the transport of water by electroosmotic mass transfer, driven by the electrical field between anode and cathode. While Na^+ ions migrate through the membrane in a hydrated state ($\sim$3–5 molecules of water per ion), the OH^- ions cannot pass through the membrane in the opposite direction. As a result, there is a net transport of water to the catholyte. The amount of water carried over into the catholyte is inversely related to the salt concentration in the anolyte.

In the design of a membrane electrolyzer with standard membranes, minimization of the voltage drop across the electrolyte is accomplished by bringing the electrodes close together. However, when the gap is very small, the voltage increases because of the entrapment of gas bubbles between the electrodes and the hydrophobic membrane. This effect is avoided in high performance membranes by coating both sides of the membrane with a thin layer of a porous inorganic material to enhance the membrane's ability to release the gaseous products from its surface. These improved membranes have allowed the development of modern electrolyzers with zero or narrow gap between the membrane and the cathode (Fig. 10). References (14,52,53) address these features in more detail.

Catalytic Cathodes. The first membrane electrolyzers introduced in the late 1970s were built with low carbon steel cathodes, a material that has been successfully used in diaphragm cells. However, since the early 1980s, the focus

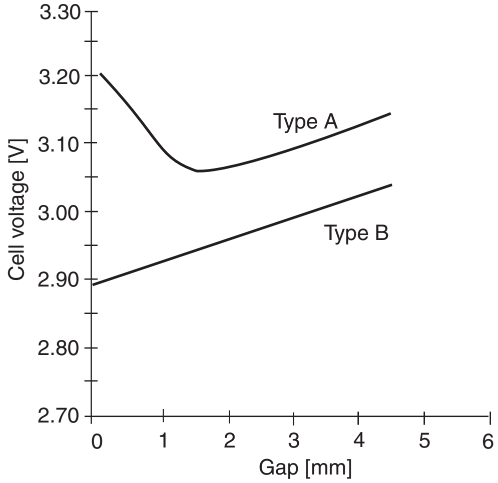


Fig. 10. Comparison conventional (type A) versus high performance (type B) membrane.

of the cathode material has been on nickel because of its stability in concentrated caustic solutions.

Depending on the electrolyzer load, the hydrogen overpotential with carbon steel cathodes is in the range of 300–400 mV. Energy savings, by reducing the overpotential as much as 200–280 mV, are realizable, in principle, by using nickel cathodes with a catalytic coating. The various approaches include using materials that provide enhanced surface area and better electrocatalytic properties than steel. Composites generally chosen for coating are based on nickel or noble metals. They are deposited on the cathode by thermal, plasma, or electrolytic routes using a second component such as aluminum or zinc, which is leached out in NaOH solutions to give a high, electrochemically active surface. Many compositions are mentioned in the literature (25,54–56). However, the coatings that are commercially employed in membrane cells include nickel–sulfur (57), nickel–aluminum (58), nickel–nickel oxide mixtures, and nickel coatings containing the platinum group metals (59). Although catalytic cathode technology is practiced in membrane cells, commercialization is still awaited in diaphragm cells. The technical problems confronting the use of catalytic cathodes in diaphragm cells include selection of a coating technique for the complex cathode assembly that would not adversely influence the structural tolerances involved in the fabrication of cathodes and developing shutdown procedures that would eliminate hypochlorite as quickly as possible to preserve the catalytic activity of the coatings. Such problems do not exist in membrane cells because of the anion rejection properties of the membrane and effective anolyte flushing procedures during shutdowns.

Electrolyzers. Electrolyzers are classified as monopolar or bipolar, depending on the manner in which an electrical connection is made between the electrolyzer elements. In the monopolar type, all anode and all cathode elements are arranged in parallel (see Fig. 11). Such an electrolyzer will operate at a high amperage and low voltage. While the amperage is set by the number of

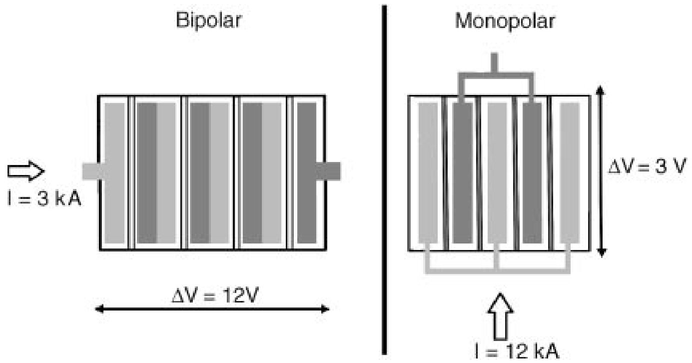


Fig. 11. Bipolar and monopolar arrangements.

elements in an electrolyzer, the total voltage depends on how many electrolyzers are in an electric circuit. In a bipolar configuration, the cathode of one cell is connected to the anode of the next cell, and thus the cells are configured in series. This scheme of cell assembly results in operation of the cells at a low amperage and high voltage. The bipolar arrangement is advantageous for realizing low voltage drop between the cells. However, problems associated with current leakage and corrosion arise in bipolar operations, since the feed and discharge streams of electrolytes to and from the cells, having different electrical potentials, are hydraulically connected via common manifolds and collectors. These problems can be avoided by properly designing the electrolyzer (eg, by limiting the number of elements per electrolyzer) to limit the overall stack voltage to a safe value. The monopolar design, on the other hand, suffers from the voltage losses occurring in the interelectrolyzer connectors. This inevitable drawback can be minimized by a conservative design. While the bipolar systems allow shutdown for maintenance of a single electrolyzer unit, independently from the rest of the plant, monopolar electrolyzers have to be designed in such a way that an individual electrolyzer can be short circuited, enabling maintenance and membrane replacement without shutting down the entire circuit. It is also possible to combine these two configurations in a hybrid electrolyzer arrangement. This has been used in conversion projects where the electrolyzers had to be configured properly to integrate with the existing rectifiers and their performance.

Commercial Electrolyzers. All membrane electrolyzers have common general design features like vertical membrane position, stacked elements and usage of similar materials of construction. Nevertheless, there are quite substantial differences in the cell design.

One of general design differences is the manner of achieving effective sealing of the electrolyzer. The most common principle is the filter press arrangement, where tightness is achieved by pressing together all elements of an electrolyzer from both ends. The relatively high sealing-forces are produced by means of hydraulic devices or tie rods. A different approach is the single element design, developed and applied by Uhde, where each element is individually sealed, by a flanged connection between the cathode and the anode semishell. The preassembled elements are stacked to form an electrolyzer, but only moderate forces are applied to ensure electrical contact.

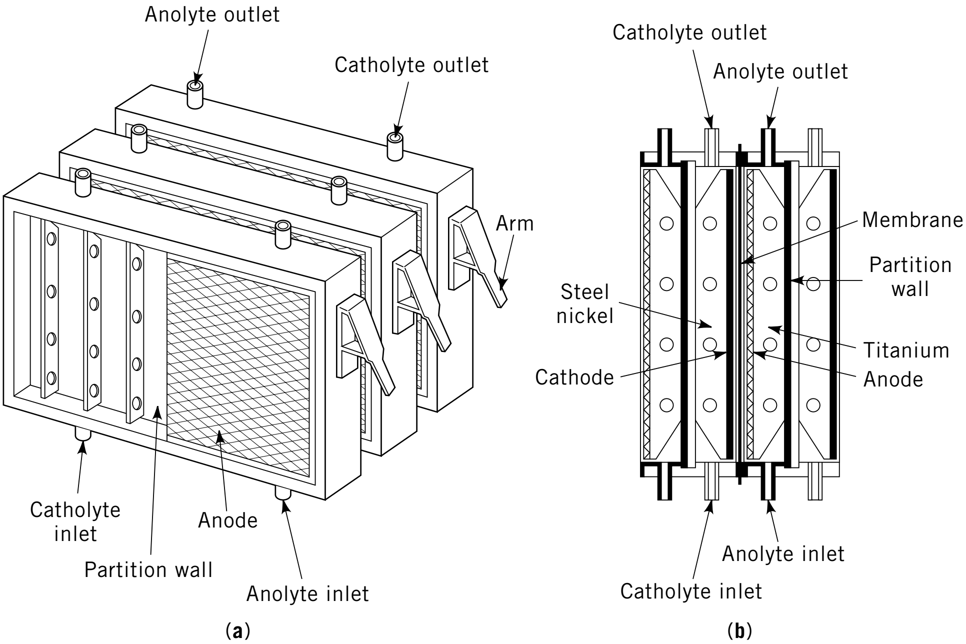


Fig. 12. Schematic of Asahi Kasei Acilyzer-ML bipolar electrolyzer. (**a**) View of cell units; (**b**) structure of cell.

As the membrane development allows increasing current densities, electrolyzer internals have to meet the related effects. Essential design targets are the minimization of structural voltage losses, homogenization of electrolyte concentration and temperature, as well as measures to counter problems related to the increased gas evolution.

The actual electrolyzer designs of the suppliers are discussed below.

Asahi Kasei Industry's Acilyzer-*ML Bipolar electrolyzers.* Asahi Kasei's electrolyzer (Acilyzer-ML), shown in Figure 12, is of the bipolar type, composed of a series of cell frames (49). Each cell consists of a pair of anode and cathode compartments facing each other, having an ion-exchange membrane in between. The anode and cathode compartments are separated by an explosion-bonded titanium-steel or titanium-nickel plate, and vertical support ribs are welded to each side of these partition walls, to which the anode and cathode mesh are spot welded in turn. Each compartment has an electrolyte inlet at the bottom and gas–liquid outlet at the top. These inlets and outlets are connected to the supply and collection headers by PTFE hoses. Both anolyte and catholyte are recirculated back to the electrolyzer from collection tanks. Deionized water is added to the catholyte collection tank to control the caustic concentration, and ultrapurified brine is added to the anolyte collection tank to control the NaCl concentration. A portion of the catholyte is drawn off and is sent to storage or an evaporator for further concentration. A portion of the depleted anolyte is drawn off and is returned to the salt dissolution and primary brine purification system. Supporting arms are attached to both sides of the cell frame, and these frames are hung on the side bars of a hydraulic press.

The electrolyzers of Asahi Kasei are offered in two sizes, each available with either natural or forced circulation. The model ML32, with an effective membrane area of 2.72 m^2, has an annual production capacity of ~15,000 tons of NaOH (100% basis), while the bigger version, ML60, has an effective area of 5.05 m^2 and an annual production capacity of 30,000 tons of NaOH (100% basis). As of 1997 a total production capacity of ~1,832,000 tons of NaOH per year has been in operation or under construction with Asahi Kasei technology.

Chlorine Engineers CME Monopolar Electrolyzers. Chlorine Engineers Corporation (CEC) (a subsidiary company of Mitsui and Company), produces the filter press type, monopolar membrane electrolyzer (60) shown in Figure 13. Uniform electrical current travels into each anode element through titanium-clad, copper-cored conductor rods and current distributors. The current distributor in the electrolyzer serves an additional role as a downcomer, helping the electrolyte self-circulate within the cell to maintain uniformly distributed concentrations as well as efficient gas release. The internal circulation is intended to eliminate the necessity for an external forced recirculation system.

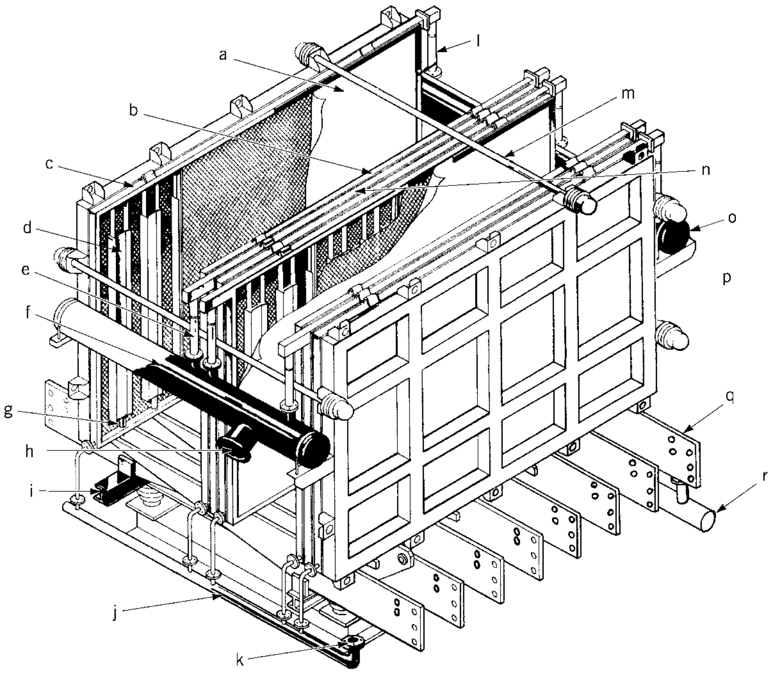


Fig. 13. CME monopolar electrolyzer: (**a**) membrane; (**b**) cathode element; (**c**) half-cathode element; (**d**) current distributor; (**e**) Teflon tube; (**f**) Cl_2 + depleted brine manifold; (**g**) conductor rod; (**h**) Cl_2 + depleted brine outlet nozzle; (**i**) base frame; (**j**) recycled NaOH manifold; (**k**) recycled NaOH inlet nozzle; (**l**) gasket (the gasket/element ratio is quite small); (**m**) tie rod; (**n**) anode element; (**o**) H_2 + NaOH manifold; (**p**) end plate; (**q**) under cell bus bar (simplifies piping around the electrolyzers); (**r**) feed brine manifold.

The gasket thickness sets the electrode spacing, and either finite or zero-gap configuration can be accomplished. The anode frame is titanium and the cathode frame is stainless steel. The CME elements are thicker than competing elements for a lower electrolyte gas void fraction. This feature minimizes the drop in the liquid level during shutdowns. CEC offers electroplated activated cathodes. Gas and liquid exit the cell in the stratified overflow mode, as the liquid level is maintained in the upper cell frame. Semitransparent Teflon tubes are used to monitor the operation visually. The electrical bus bars are installed underneath and at a right angle to the cell elements, requiring no equalizer between electrolyzers. The bus bar can be used as a short circuiting element by changing the connections. As of 1997, the installed capacity with these cells was 2,500,000 mtpy of chlorine.

Chlorine Engineers MBC electrolyzer. Chlorine Engineers retrofitted ELTECH's MDC monopolar diaphragm cell electrolyzers to convert them into membrane cells (61,62). In retrofitting, CEC installs the membrane in the form of a bag that encloses the anodes (membrane bag cell). In the MBC-29 shown in Figure 14, one bag encloses two anodes. The current conductor bar of the anode passes through a hole in the bottom of the membrane bag for connection to the base. The open end of the bag, facing upward, is fixed to the partition plate by a sealing plug.

CEC BiTAC-800 Electrolyzer. The Chemical Engineers Corporation (CEC) adapted a bipolar electrolyzer first developed by Tosoh Corporation. The electrolyzer is of the filter press type and has an effective membrane area of $\sim$3.3 m^2. Up to 80 element frames can be assembled together by spring-loaded tie rods. The electrode frames are made of a special titanium alloy on the anode side, and nickel on the cathode side. The wave-like structure of the

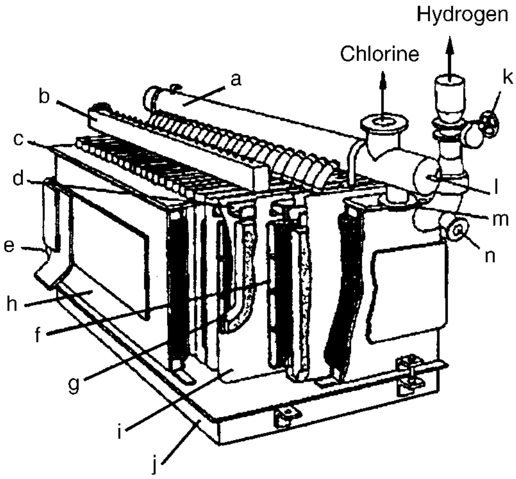


Fig. 14. Cut view of Chlorine Engineers membrane bag cell: (**a**) manifold; (**b**) frame; (**c**) partition plate; (**d**) sealing plug; (**e**) recirculated NaOH inlet; (**f**) cathode; (**g**) anode; (**h**) cathode pan; (**i**) membrane bag; (**j**) base; (**k**) butterfly valve; (**l**) feed brine; (**m**) depleted brine; (**n**) caustic-outlet.

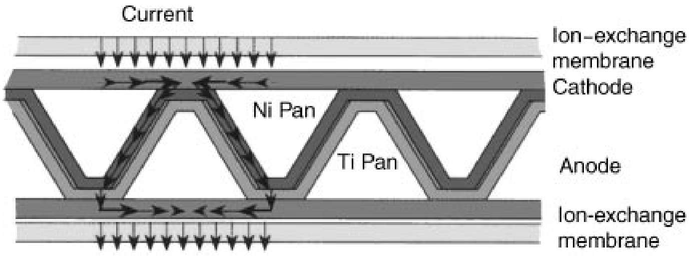


Fig. 15. Cross-section view of a BiTAC element.

cathode and anode pan serves the combined functions of partition plates and conductor ribs, as shown in Figure 15.

The current is led to the anode mainly through nickel to avoid the ohmic losses from the poor electrical conductivity of titanium. The feed and exit streams leave the cells by overflowing into the collecting pipes located at each side of the electrolyzer via external flexible hoses. The membrane cathode gap can be adjusted from zero to a finite value, to meet the requirements of various commercial membranes.

Ineos FM21-SP Monopolar Electrolyzer. Ineos' FM21-SP monopolar electrolyzer (see Fig. 16) incorporates stamped electrodes. The anode assembly is composed of 2-mm thick titanium panel between compression molded joints of a special cross-linked EPDM elastomer which is a terpolymer of ethylene, propylene, and diene. The cathode assembly consists of a 2-mm thick nickel panel between compression molded joints, also of EPDM.

The anodes and cathodes are assembled between two end plates, up to 60 anodes in the FM21-SP and up to 90 anodes in the larger FM-1500. A key feature of both designs is the elimination of any external piping to the individual cell

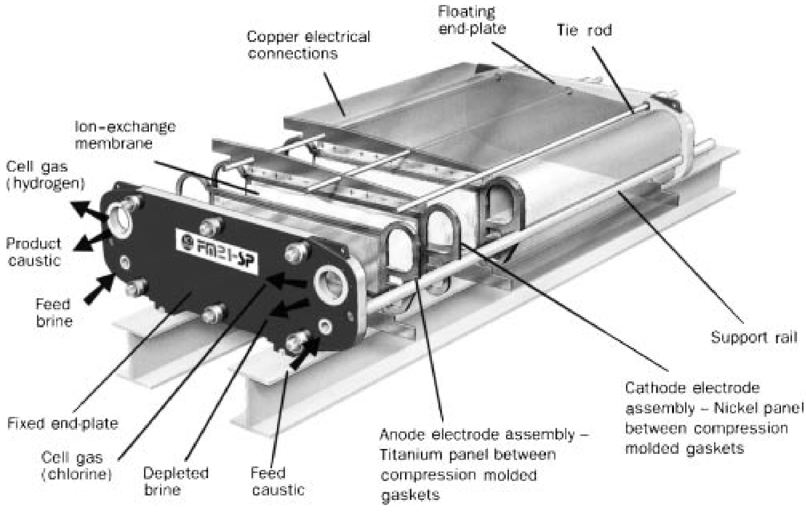


Fig. 16. Electrolyzer FM21-SP by Ineos.

compartments by the use of a simple but effective internal manifold arrangement. As shown in Figure 16, the anode and cathode panels are designed to form feed and discharge channels when assembled.

The electrolyzer has coated titanium anodes while the cathodes are made of pure nickel, either plain or coated with activated coatings. Both electrodes are pressed from integral sheets of pure metal, and this makes recoating of the electrodes simple and cost effective. Recoated structures can be sent to site prior to electrolyzer refurbishment from a pool of electrodes kept in stock by the electrode supplier for all customers. The removed, worn out electrodes are recoated without interfering with plant operations and are added to the pool of electrodes.

The effective electrode area of one monopolar cell is 0.21 m^2, which makes this electrolyzer very compact (63). The individual, lightweight electrodes are easily handled without the need for lifting devices, and this allows the electrolyzer to be rebuilt or refurbished in a short time.

ELTECH ExL Electrolyzers. ELTECH offers three electrolyzers called ExL^M, ExL^B, and ExL^{DP}. The monopolar ExL^M is the modified version of the earlier MGC electrolyzer (membrane gap cell) (64). Improvements have been made to the anode and cathode design and fabrication techniques, as well as to the gasket and manifold materials. This has resulted in a uniform current distribution across the active membrane area and increased internal circulation. One of the main features of this cell is the double-gasket design. The cathode O-ring is located closer to the liquid than the anode O-ring, which is not in permanent contact with the chlorinated brine, thereby serving as a well protected back up seal. The general cell design is of the filter press type, where the elements are pressed together by tie rods with copper distributors. The intercell connections are from the sides, and the support for the electrolyzer is the copper current redistribution bus between each electrolyzer. The feed streams and products enter and leave the element via the attached manifold devices. Up to 30 membranes with an effective area of $\sim$1.5 m^2 each, can be put together in one electrolyzer providing a production capacity of 9.3 tons of NaOH per day (100% basis) The maximum current density is 7 kA/m^2.

The model ExL^B (Fig. 17) is the bipolar version of the ExL^M. The bipolar arrangement is realized by pressing the nickel cathode pan onto the nickel plated back of the anode pan. Up to 60 elements can be combined in one electrolyzer, to realize a production capacity of 29 tons of NaOH per day (100% basis).

The ExL^{DP} electrolyzer (dense pak) represents a hybrid cell arrangement, combining multiple ExL^B type electrolyzer blocks, each consisting of 2–10 elements, in one electrolyzer unit. The blocks are electrically separated from each other using standard monopolar components.

Uhde Bipolar Electrolyzers, Single Element Design. The characteristic feature of the Uhde membrane electrolyzer is its single element design (65). Each element mainly consists of an anode and a cathode semishell separated by an ion-exchange membrane. Unlike the filter press design concept used in other electrolyzers, each element is individually sealed by means of a separately bolted flange with gasket. This enables a long term storage of fully assembled elements in working order. The elements are suspended on to a steel rack and are pressed together to establish a good electrical contact. High forces are not required to achieve effective sealing in the single-element concept. Up to 160 single elements

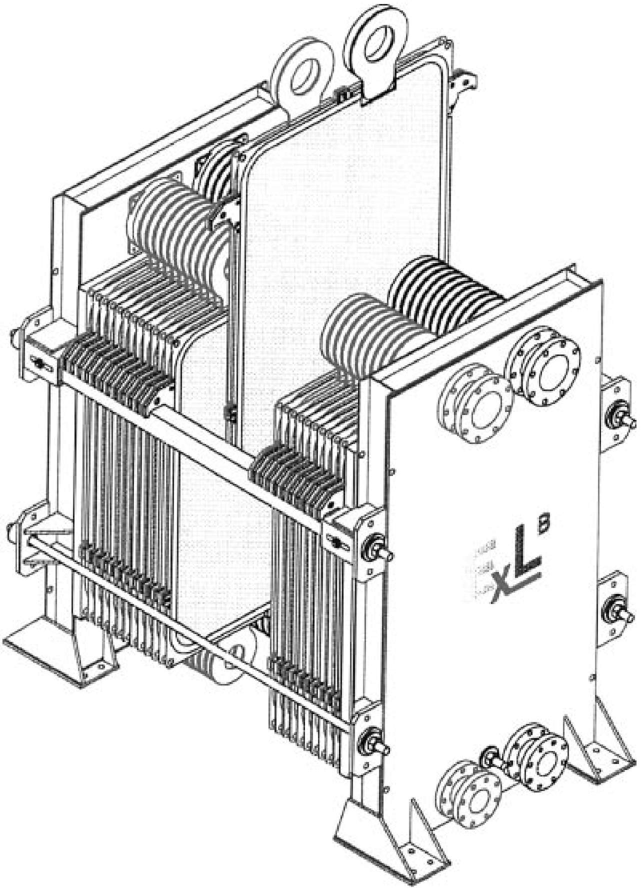


Fig. 17. Electrolyzer ExL^B by ELTECH.

can be combined in one electrolyzer as shown in Figure 18. Currently, single elements of the third generation, as shown in Figure 19, are used. The standard electrolyzer configuration is the bipolar arrangement, although monopolar or hybrid arrangements can be made, as needed by the customer.

The current passes from the back of the cathode wall from one element to the back anode wall of the subsequent element by a series of contact strips. Voltage losses are reduced by means of a laser welded, direct connection between the outer contact strips and, via vertical inner-current conducting plates, the electrodes. Both brine and caustic enter the element via flexible hoses leading to horizontal inner distribution pipes. These provide uniform feed concentration profiles inside each compartment. Internal circulation is achieved and enhanced by two baffle plates located in the anode compartment. The upper, inclined baffle plate provides a constant exposure of brine to the membrane, thereby avoiding the gas-phase blistering of the membrane. In addition, the vertical baffle plate contributes to the uniformity of both, temperature and concentration profile in the compartment.

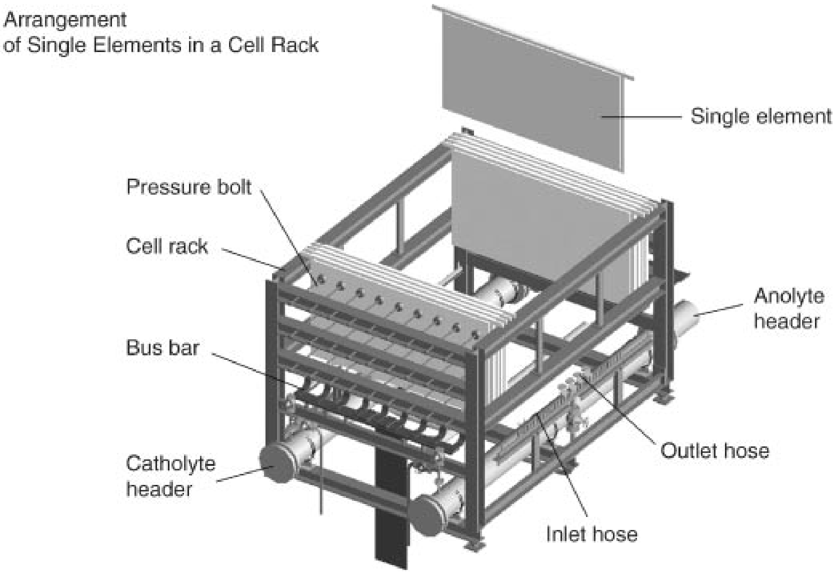


Fig. 18. Krupp Uhde BM-2.7 electrolyzer.

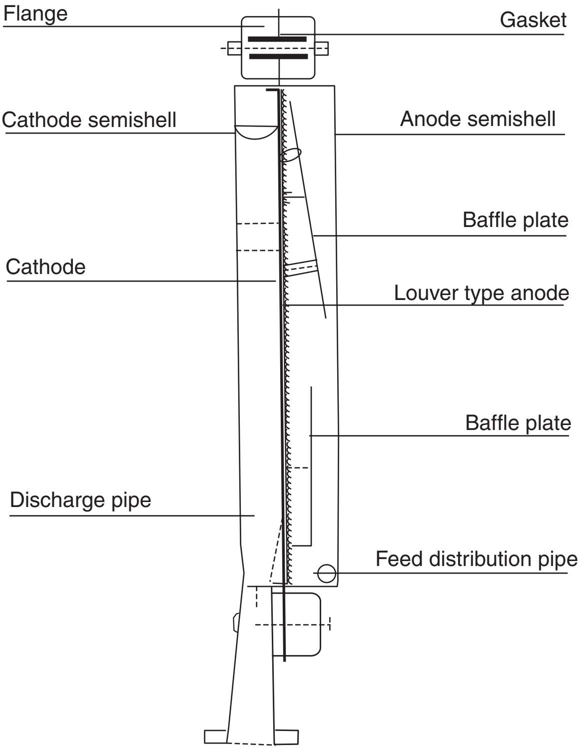


Fig. 19. Uhde single element, third generation.

The product gases leave the element together with the electrolyte downward via vertical discharge pipes and exit to the collectors via flexible PTFE hoses. All inlet and outlet connections are located at the bottom of the electrolyzer, releasing the space above the cell for maintenance purposes. The mesh-type anode serves as a support for the membrane while a defined gap is maintained between the louver type cathode and the membrane by spacing devices.

The typical electrode active area is 2.7 m^2 (1.8 m^2 also available) and the annual electrolyzer production capacity can be up to 28,000 tons of NaOH (100% basis, with electrolyzers having 160 elements at 6.0 kA/m^2). In 2002 Uhde had 70 plants with a total annual capacity of ~4,800,000 tons of NaOH (100% basis) commissioned or under construction. About one-third of this capacity has come from conversion projects from mercury or diaphragm plants to membrane technology (65). A summary of the current membrane cell technologies is provided in Table 5.

Membrane Cells with Oxygen or Air Depolarized Cathodes. Substituting an oxygen reduction reaction for the hydrogen evolution reaction at the cathode in chlor-alkali electrolysis will reduce the total cell voltage by ~1 V (theoretically 1.23 V), thereby realizing a substantial saving of electrical energy (66). Figure 20 depicts a schematic of a membrane cell operating with an air-depolarized cathode, referred to as a “Gas Diffusion Electrode” (GDE).

The anode reaction is the same as in a conventional chlor-alkali cell, where the chloride ions are discharged to form chlorine gas product and the sodium ions migrate to the cathode compartment through the ion-exchange membrane. At the cathode, oxygen is reduced to the OH^- ions, which combine with the Na^+ ions to form sodium hydroxide. The oxygen consumed in this reaction enters the air cathode compartment either as water-saturated pure oxygen gas or as

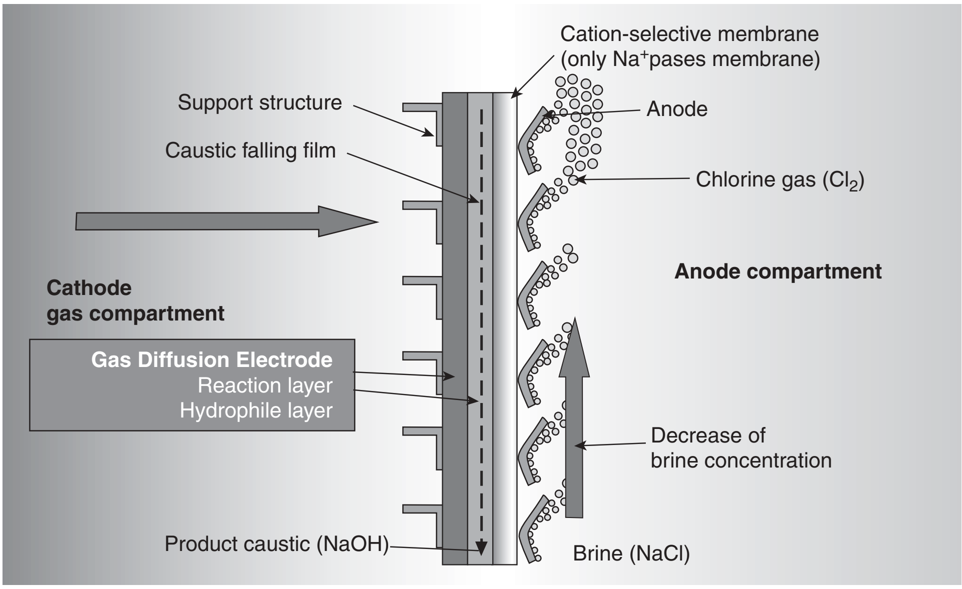


Fig. 20. Schematic cross-section through a GDE cell, falling film type (67).

air and gets reduced at the porous air cathode. The advantages of using the oxygen reduction reaction include avoidance of costly downstream treatment of hydrogen and absence of the gas void fraction in the catholyte, resulting in a reduced ohmic drop in the cell. However, this scheme requires a high performance air scrubbing system to remove all carbon dioxide from the air in order to protect the air cathode from the accumulation of sodium carbonate and a premature failure of the cells. As the anode side of the process does not differ from the conventional chlor-alkali cell, those components can be used without any modifications.

The cathode reaction for this system is

$$2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^-$$

giving a standard potential 1.23 V lower than that of the decomposition voltage of water to hydroxide ion and hydrogen. Pilot electrolyzers have operated at <2.5 V at a current density of 6 kA/m^2 (67).

The cathode side has several special requirements, the central one being the adjustment of the local differential pressure between the caustic and the oxygen compartment on the other side of the electrode. Due to the porous nature of the GDE, a pressure balance across the electrode has to be established in order to avoid the flow of the fluid from one side to the other. As shown in Figure 21, there is a certain tolerance range of the differential pressure, where the electrode works properly.

The local differential pressure is a function of height, because of the different densities of the fluids, and can be made small using two different approaches. The first one involves splitting the cathode compartment into several horizontal compartments, called gas pockets in which the height of each subcompartment limits the hydrostatic pressure of the caustic to a tolerable value. The lean caustic flows through the pockets successively, by overflowing from one pocket to the next one below. This gas-pocket principle (see Fig. 22) is patented and now

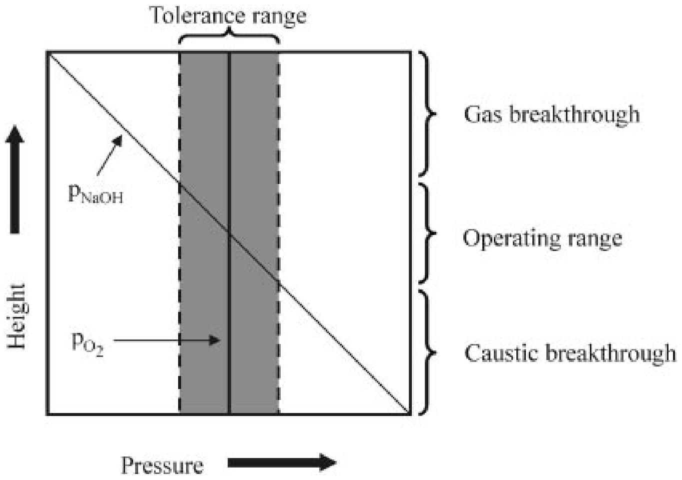


Fig. 21. Differential pressure over a porous GDE-type electrode (51).

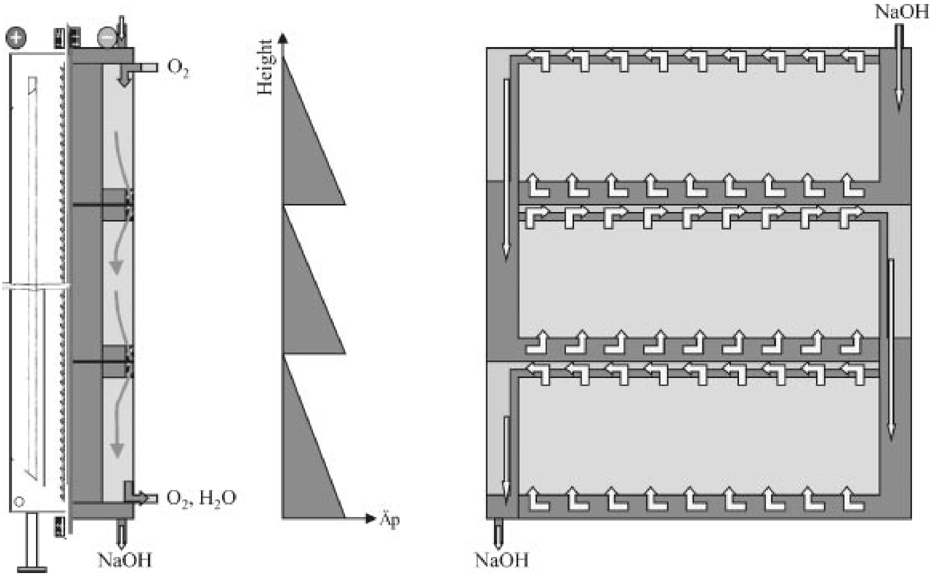


Fig. 22. Gas-pocket type GDE element.

being tested by the Bayer AG group (68). A second approach to the problem is the falling-film principle (see Fig. 23). The development of this type was initiated by the Hoechst group in the 1980s (69–72), but is presently continued by Uhde. The idea here is to decrease the hydrostatic pressure of the caustic successively by establishing a falling film of caustic between the electrode and the membrane. This is realized by means of a layer of hydrophilic material that is fixed between the anode and the cathode. This design ensures a constant gap between the GDE and the membrane itself. Because of the electroosmotic water transport from the anolyte to the catholyte, the caustic flow increases from the top to the bottom of the cell. A high flow in the hydrophilic layer will lead to a flooding of the GDE, and hence a breakthrough of caustic into the oxygen compartment, caused by the increased differential pressure. This flooding can be avoided by a proper design of the hydrophilic layer. The falling-film technology shows some inherent advantages. Unlike the gas-pocket principle, the falling-film technology does not need an extensive gasket system throughout the surface of the GDE, thereby allowing a simplified design. Furthermore, the GDE can be run close to atmospheric pressure, so it will always operate in the optimum operating pressure range. Both processes show comparable operating data. However, they are still at an experimental level. Nevertheless, the initial results with the GDE system are promising toward achieving energy savings of ~30% compared to the conventional membrane process.

Figure 24 gives an overview of the evolution of the specific energy consumption of membrane cells. The remarkable improvement in performance reflects the progress made in membrane development and electrolyzer design. This has reduced operating costs by reducing voltage losses and optimizing current efficiencies. Furthermore, the operating current density has been doubled from

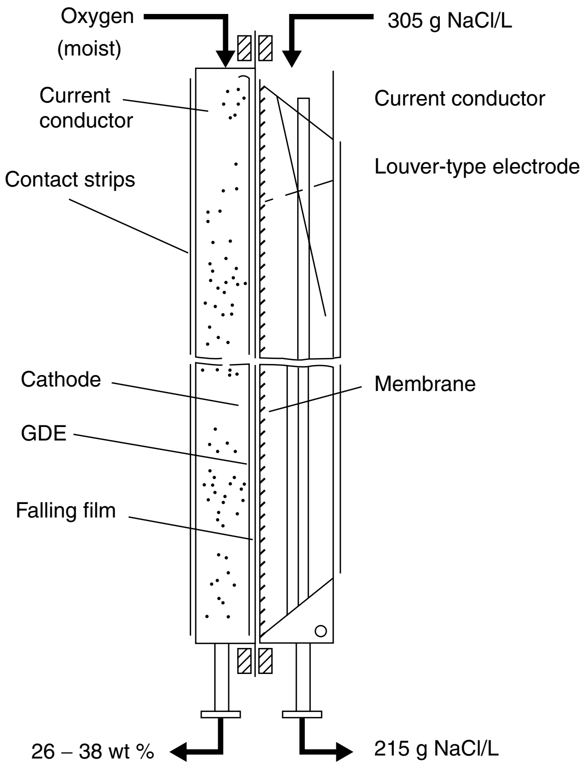
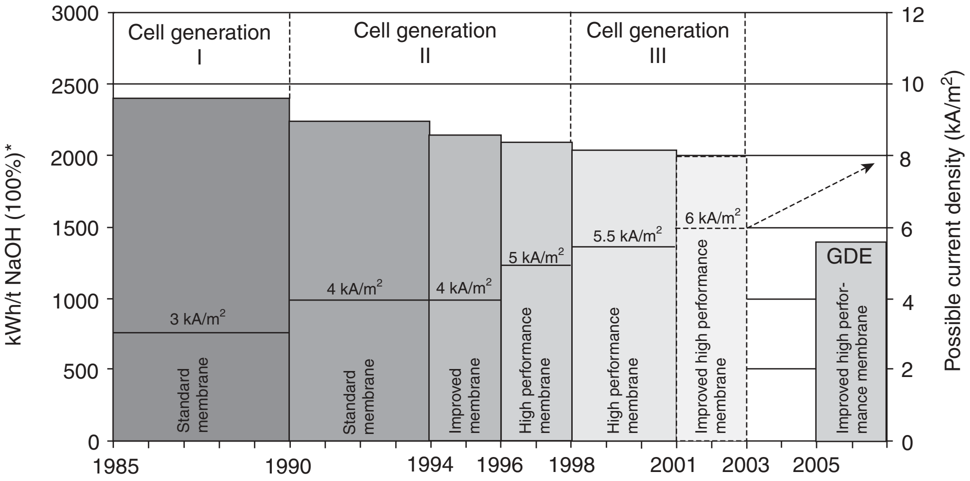


Fig. 23. Falling-film type GDE element (65).



*expected figures for commioning and 4 kA/m^2

Fig. 24. Evolution of energy consumption and current density for Uhde membrane technology (67).

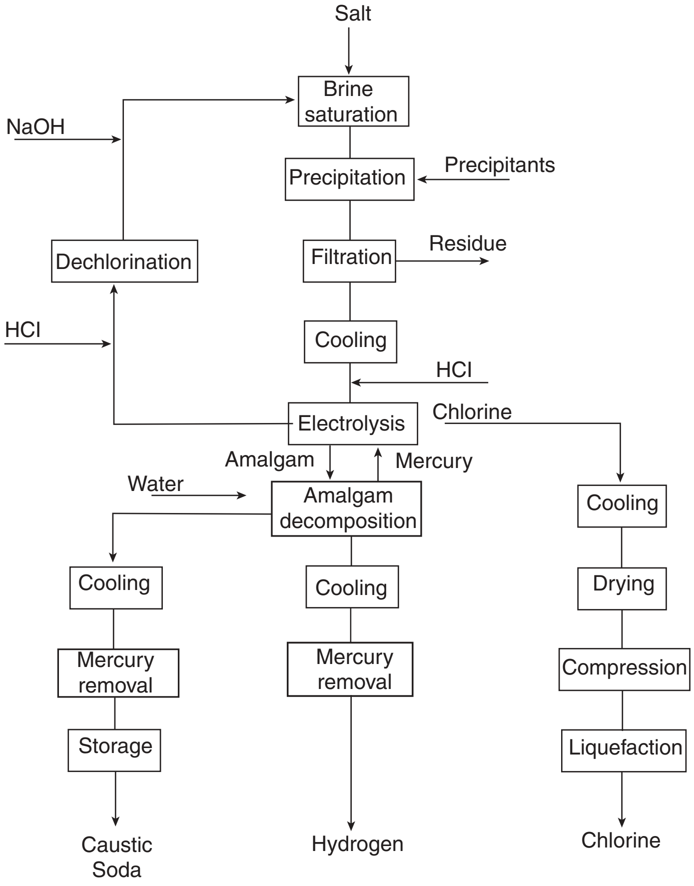


Fig. 25. Flow diagram of the mercury cell process.

3 to 6 kA/m^2 over the past 20 years, reducing the capital costs associated with the electrolyzers.

4.5. Chlorine Plant Auxiliaries. The auxiliary systems for each of the three electrolytic chlor-alkali processes, depicted by block flow diagrams (Figs. 25–27). Although they differ somewhat in operation, the processes of brine purification and chlorine recovery are common to each.

Brine Preparation. There are several different major sources of the fundamental raw material, sodium chloride. It can be recovered from underground rock salt deposits. Methods of recovery include conventional mechanical mining, which has much in common with the mining of coal, and solution mining, in which water or weak brine is forced into a salt deposit to dissolve the material and carry it back to the surface. The former typically costs about twice as much as the latter (73). Salt is also obtained by evaporation of saline waters. Ocean water, for example, contains ~3.5% NaCl. Inland sources may be more concentrated and may contain other minerals of greater value. The Dead Sea and the Great Salt Lake are examples. The salt obtained from these waters is

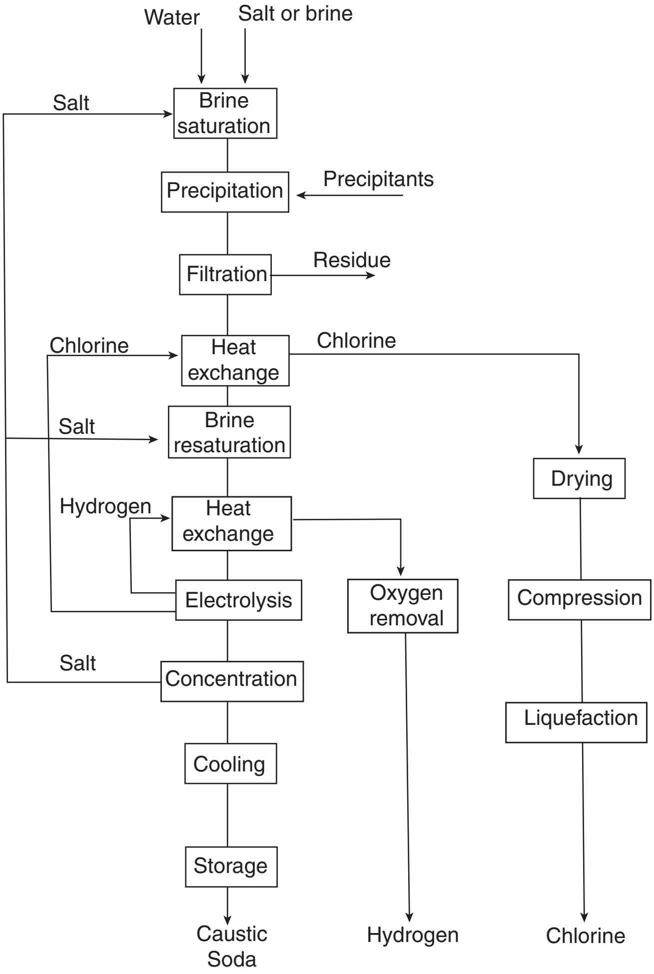


Fig. 26. Flow diagram of the diaphragm cell process.

usually referred to as solar salt, since solar energy provides the driving force for evaporation. There are also surface or near-surface deposits of salt and wild brines near the surface of the earth, but these are relatively minor sources.

However obtained, sodium chloride will have a characteristic set of impurities. The major impurity in nearly all salts is some form of calcium sulfate. While compositions from different sources vary widely, a few generalizations can be made. Solar salt, at least after the common operation of washing, is usually purer than rock salt. It is also more susceptible to caking and mechanical degradation. While rock salt contains more calcium sulfate, it contains in proportion less magnesium. The higher ratio of calcium to magnesium improves performance in the brine treatment process.

Many chlorine plants operate with salt that has already undergone some purification. Most solar salts, eg, are washed to remove occluded liquor and surface impurities. Another example is vacuum purified salt, which is recrystallized

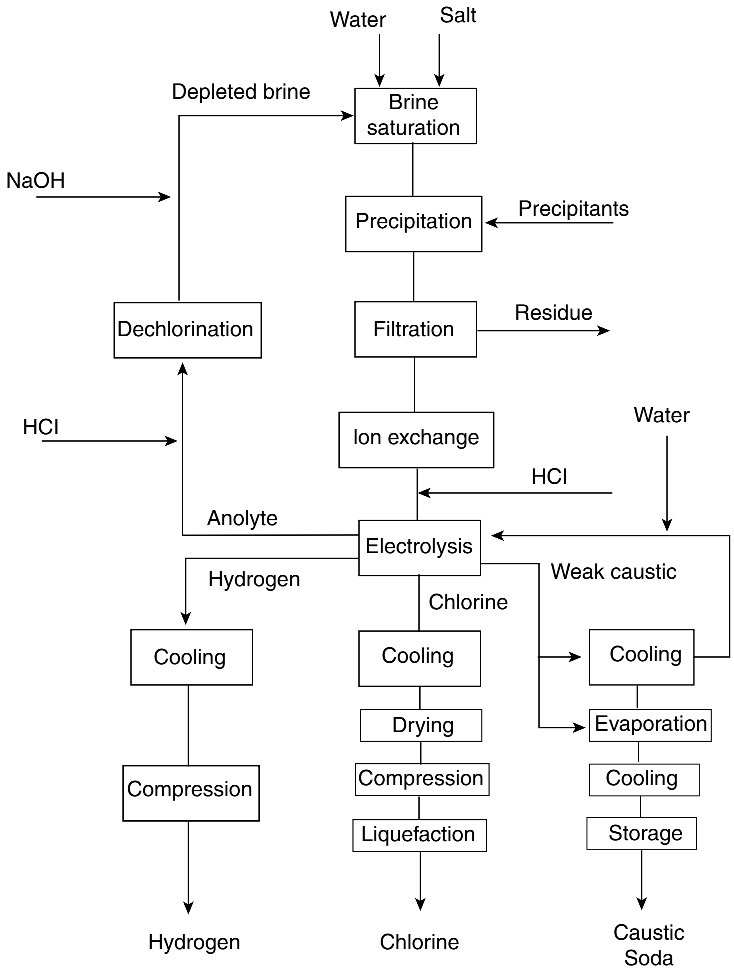


Fig. 27. Flow diagram of the membrane cell process.

from brine after most of the impurities have been removed by chemical treatment. Table 6 shows typical analyses of the three types of salt discussed above.

The salt may be delivered to a plant as the solid or already dissolved to give a raw brine. Solution-mined material is an example of the latter. As the flow diagrams and the process descriptions that follow will show, only the diaphragm-cell process can operate with a brine feed without special design. When solid salt is

Table 6. **Comparison of Purity of Various Types of Salt**[a]

Component	Rock salt	Washed solar salt	Vacuum salt
sodium chloride	93–99	99	99.95
sulfate	0.2–1	0.2	0.04
calcium	0.05–0.4	0.04	0.0012
magnesium	0.01–0.1	0.01	0.0001

the raw material, a dissolving operation becomes necessary. The partially depleted brine from mercury or membrane cells is recirculated and resaturated with the fresh salt. Handling and dissolving are not technically complex operations, but their scale can be large. A 1000-tons/day chlorine plant requires ~1700 tons/day of salt. Much of the detail in saturator design has to do with the behavior of the solid particles as they continuously become smaller and the removal and handling of undissolved impurities (74).

Brine Purification. Impurities in the brine can affect the performance of any type of cell. The most common cationic impurities, and those present in the greatest concentrations, are the hardness elements, calcium and magnesium. In diaphragm and membrane cells, these can precipitate as the hydroxides when exposed to a sufficiently high pH, which occurs within the diaphragm or membrane as the ions approach the catholyte side. Membranes are especially sensitive to brine impurities, and the membrane-cell process requires a higher degree of brine quality than does either of the other technologies. Where the hardness specification for the brine fed to a diaphragm cell may be ~5 ppm, an efficient membrane cell will require a level of no greater than 20 ppb. Elements whose oxides can form insoluble complexes, particularly in the presence of calcium, also must be controlled. These include silicon and aluminum. Iodine, too, can form the highly insoluble sodium paraperiodate, $Na_3H_2IO_6$ or interact with barium. Table 7 compares the brine specifications for membrane and diaphragm cells. Membrane-cell specifications in particular vary with service conditions and supplier's requirements. Some specifications change with operating current density, and some are interrelated (eg, some cell suppliers allow higher strontium content if the silica level is quite low).

With a different operative mechanism in mercury cells, the same impurities do not cause permanent damage to the chlorine/caustic separator. Instead, traces of metals such as vanadium, molybdenum, chromium, iron, titanium, and

Table 7. **Typical Specifications for Feed Brine to Electrolyzers**

Component	Membrane process[a]	Diaphragm process[a]
sodium chloride	290–310 g/l	320 g/L[b]
calcium and magnesium	20 ppb	5 ppm
sodium sulfate	7 g/L	5 g/L
silica	5 ppm	0.5 ppm
aluminum	0.1 ppm	0.5 ppm
iron	1 ppm	0.3 ppm
mercury	0.5 ppm	1 ppm
heavy metals	0.2 ppm	50 ppb
fluoride	0.5 ppm	1 ppm
iodine	0.2 ppm	
strontium	0.5 ppm	[c]
barium	0.5 ppm	[c]
total organic carbon	1 ppm	1 ppm
pH	2–11	2.5–3.5

[a] All ppm and ppb values represent maximum concentrations allowed.
[b] Minimum.
[c] Included with calcium and Magnesium.

tungsten must be avoided. These metals lower the hydrogen overvoltage at the mercury cathode and permit increased formation of hydrogen. This lowers the current efficiency and creates a hazard in the processing of chlorine.

Impurities that are soluble in the acidic anolyte can become insoluble once they have entered the membrane. In addition to the induced flow of cation impurities, neutral and anion impurities can enter by diffusion and by the considerable water flow from anolyte to catholyte. Internal precipitation of these impurities disrupts the structure of the membrane. This precipitation can increase the voltage drop through the membrane. If it occurs in the cathode-side layer, it will reduce the selectivity of the membrane and therefore the current efficiency of the cell. Even if the impurity is subsequently washed out, the void left behind still contributes to reduced current efficiency. There also are synergistic effects, such as the precipitation of complex compounds, usually involving calcium and magnesium in combination with silica and alumina.

The most important anionic impurity, because of its widespread distribution in salt, is sulfate. Its control becomes increasingly more important as cell technology advances. Refined salts can be purchased at a premium to reduce the magnitude of the problem; sulfate can be preferentially rejected in the dissolving process; or it can be removed from the brine by precipitation, ion exchange, or nanofiltration. There is a growing literature on the subject, much of it available in the General References.

Some brines also contain ammonium ions or organic nitrogen that can be converted to the explosive nitrogen trichloride. Ammonium ions in the brine are removed by treatment with chlorine or hypochlorite. Depending on its severity, this treatment produces NH_2Cl, which can be removed as a gas. Brine purification represents a significant part of chlor-alkali production cost, and this is especially so in the membrane process, with its stringent requirements. Moreover, part or all of the depleted brine from mercury and membrane cells must be dechlorinated before recycle to the cells, at further expense. Further discussion of this operation is noted below.

Brines are treated with Na_2CO_3 to precipitate calcium carbonate and with NaOH to precipitate metal hydroxides, notably that of magnesium. The brine may be heated before treatment to shorten the reaction time and improve the subsequent precipitation and settling of the solids. Calcium carbonate tends to form a dense, coherent precipitate, while magnesium hydroxide forms a floc that is light and fragile. The $Mg(OH)_2$ precipitates can be degraded by agitation and tend to settle slowly. When the two metals are precipitated together, hybrid particles form, and the calcium helps the magnesium to settle more quickly. When the calcium to magnesium ratio is low, the calcium carbonate precipitate is not able to assist settling of the magnesium hydroxide floc. In such cases, flocculants are sometimes added to the brine. These typically are polyelectrolytes that are able to bind together the light, fluffy $Mg(OH)_2$.

After carbonate and caustic treatment, the precipitates settle in a clarifier, where most of the solids are removed as a mud. This mud can be processed further to increase its solid content and to recover most of the occluded chloride. The overflow from the clarifier contains a few tens of ppm of solids, which are removed by filtration. The first step of filtration usually is in beds packed with sand or, particularly in membrane-cell plants, non-siliceous materials such as anthracite or garnet. Most modern plants use pressure filtration, and flow may be up or down through the beds. Precoated polishing filters follow this primary filtration. Leaf and candle filters are common. In membrane-cell plants, it is even more important to avoid siliceous materials in this step, because those in the form of filter aids are amorphous and are more easily soluble. Cellulosic materials are the usual substitute. Membrane-based filters with controlled pore sizes are able to function in this application without filter-aid. Use of sharp backpulse of brine after deposit of small quantity of solids keeps the filter surface clean and functional.

After filtration, brine usually contains <5 ppm hardness and is suitable for the mercury and diaphragm processes. The membrane process, however, requires brine with <20 ppb hardness, which requires another purification step, based on ion exchange. The resins used have the standard styrene–divinylbenzene backbone, but special exchange groups are necessary. The process is one of softening by replacing undesirable multivalent cations in the brine with sodium or potassium. Because of the extremely high concentration of the latter ions in the brine, standard resins do not have the selectivity required for efficient removal of the other ions. The types used in this application therefore have either iminodiacetate or aminophosphonic pendant groups (See Reference 72). The alkaline brine from the filtration plant passes through beds packed with such a resin. The process is cyclic, with bed regeneration by HCl, to strip off the metal ions, and NaOH, to restore the resin to its active form.

The brine fed to the electrolyzers in all processes is usually acidified with HCl. This neutralizes residual hydroxide and carbonate in the brine and prevents their reaction with chlorine formed at the anodes. The formation of by-products such as oxygen and chlorate is reduced in this way. Excess acid also can react with hydroxyl ions that leak back from the catholyte to the anolyte in the cells. This again reduces oxygen formation and provides a purer gas, and so it serves as a technique for producing chlorine gas suitable for direct use in its primary outlet, the synthesis of ethylene dichloride. Over-acidification in a membrane-cell plant, however, can reverse the hydrolysis of the carboxylate groups that provide high ion selectivity in the membranes. The resulting formation of the non-conductive carboxylic acid form renders the membranes inactive. The process of acidification must be closely monitored to prevent this adverse effect.

As mentioned above, the depleted brine issuing from membrane or mercury cells must be recycled. Dissolved chlorine must first be removed. Most of the chlorine present is in the hydrolyzed form of hypochlorite:

$$\mathrm{Cl_2 + H_2O \leftrightarrow H^+ + Cl^- + HOCl} \tag{17}$$

Addition of HCl to the brine reverses the reaction, and the molecular chlorine formed is much easier to remove, usually by application of a vacuum. There is a certain residual concentration after this dechlorination process, and in a membrane-cell plant it must be removed to protect the ion-exchange resin from oxidation. This is done chemically by addition of a reducing agent, which typically is hydrogen peroxide or a reacted form of SO_2. The product of the reaction is the innocuous chloride ion. When sulfite is the reducing agent, the reaction is

$$\mathrm{SO_3^{2-} + OCl^- \rightarrow SO_4^{2-} + Cl^-} \tag{18}$$

In a mercury-cell plant, on the other hand, complete dechlorination is undesirable, because a certain amount of free chlorine in the circulating brine solubilizes mercury and prevents its loss from the system along with the brine treatment sludge. The chemical dechlorination step therefore is omitted.

Chlorine Processing. The first step in the chlorine-handling process is the cooling of the gas, which is saturated with water at cell operating temperature. Most cells operate very close to atmospheric pressure, although membrane cells have the capability to run under positive pressures, up to several hundred kilopascals. Direct- and indirect-contact cooling is used. Direct cooling was more common in the past, when metals resistant to wet chlorine gas were not economically available. In this process, the gas from the cells is contacted with a countercurrent stream of brine or cooling water in a column. Indirect exchangers are single-pass devices with titanium tubes and carbon steel shells. Titanium plate exchangers are used in some smaller plants.

Cooling the chlorine incidentally removes most of the water by condensation. Lower temperatures promote the removal of water and reduce the consumption of drying acid in the next step of the process. Particularly in large plants, the use of two coolers in series is common, with the second operating on chilled water. There are, however, basic limitations on the degree of cooling that can be safely applied. At atmospheric pressure, eg, a solid hydrate of chlorine forms at temperatures below 9.6°C. The group of gas hydrates that includes chlorine forms unit cells of forty-six water molecules; the composition of the hydrate is $Cl_2 \cdot nH_2O$, where the value of n usually is taken to be between 7 and 8. Cotton and Wilkinson (75) estimate $n = 7.2$ or 7.3. This hydrate deposits in equipment, disrupting operation and creating a hazard. In titanium equipment, another limitation is the loss of the protective oxide film that prevents reaction between chlorine and the metal when the partial pressure of water is too low. Work sponsored by Euro Chlor (76,77) suggests that the temperature of the gas at atmospheric pressure should not be taken below ~13°C. This result is consistent with other work (78) that indicates that a concentration of 1.0–1.5% water vapor is sufficient to maintain the film.

The water condensed in the cooling process is saturated with chlorine. Chlorine can be removed from this water by acid-assisted vacuum stripping. In a mercury- or membrane-cell plant, the water can be combined with the depleted brine and the two treated together. Diaphragm-cell plants, with no depleted brine recycle, require addition of a dedicated stripper to handle the condensate. The process is basically the same, but the lack of salt in solution means that the chloride ion concentration is lower. As reaction 17 will make clear, more acid must then be added to reverse the hydrolysis reaction and reduce the solubility of chlorine.

After the gas is cooled, the next step in the process is its drying. Concentrated sulfuric acid (93–98%) removes the remaining water, producing a spent acid. Depending on further use or the method of disposal, the strength of this acid may range from 50 to 80% H_2SO_4. Drying takes place in columns that usually provide two to four theoretical stages. Outlet moisture specifications usually are <50 ppm (v/v). Both plate and packed columns are used; some columns are hybrid, with plates mounted above a packed section. Because of the very low net throughput of acid, packed columns require circulation of acid over the beds. The circulating acid can be cooled to remove the heat of absorption of water. Multiple beds may be installed in a single column, or separate single-bed columns may be used. The flows of gas and acid through the columns are countercurrent.

Packed columns in large plants have been built of brick-lined steel, with glass fiber membranes between the bricks and the wall. In smaller units, FRP (fiber-reinforced plastic) is a common material, and this is often reinforced with PVC. In the last stage of drying, where the acid concentration is essentially that of the feed material, unlined carbon steel frequently is used. Ceramic and plastic packing are common, and support and hold-down plates may be ceramic or coated steel.

The dry chlorine gas issuing from the drying system and the wet gas issuing from the cells both contain fine particles in the submicron to ten-micron range. Particles of such small size by definition constitute a mist. In the case of dry gas, the particles are droplets of concentrated sulfuric acid. In the case of wet gas, the particles are those of solutions of salt and sometimes caustic soda. In both cases, the mist can deposit in downstream equipment. Normal practice is to remove these particles before allowing the gas to travel forward from the operation in question. Conventional inertial impact mist eliminators are not highly effective against mists. The standard apparatus therefore contains candles wrapped with a porous fiber. This fiber is tightly constructed and forces the gas through a narrow, tortuous path. The mechanism of collection of the finest particles depends on their Brownian motion. The vessels containing the demisting elements are carbon steel in the case of dry chlorine and FRP or lined steel in the case of wet chlorine (79). The elements are glass in stainless steel mesh enclosures (dry chlorine) or glass or polyester in FRP or PVC enclosures (wet chlorine).

After drying, chlorine usually is compressed to a higher pressure. This compression is done to allow liquefaction of the gas or to deliver it to another process (eg, production of ethylene dichloride). Compressors may be centrifugal, liquid-ring, or reciprocating. The centrifugal compressor is the standard in large plants. Several stages of compression usually are necessary to reach the desired pressure. Because of the combustibility of chlorine in contact with the ferrous metals used in compression systems, temperatures must be strictly limited. Failure to do this has been the cause of a number of fires. Temperatures are limited by mechanical design and by coolers placed before compression and between stages of the compressor.

Centrifugal compressors have a number of advantages in this service, including relatively compact size, high mechanical efficiency, smooth operation, and outstanding reliability. The last of these allows them to be used in many plants without installed spare capacity. Disadvantages include the mechanical demands of their high rotational speed, the complex lubrication and sealing systems required, and the fact that performance depends on molecular weight of the gas. Centrifugal machines also are subject to surge, and hence surge control is an important part of system design.

Liquid-ring compressors in chlorine service are sealed with concentrated sulfuric acid. They are limited in size and have relatively low mechanical efficiencies. Because the rotating acid ring absorbs some of the heat of compression, they are able to operate at higher compression ratios than the other types of compressor without developing dangerous temperatures. Frequently, then, single-stage machines can deliver chlorine directly to the liquefaction process. Before the advent of the centrifugal compressor, a number of fairly large plants depended on batteries of liquid-ring machines. These have gradually converted their operation to the centrifugal type, and the liquid-ring type today is found primarily in smaller plants.

Reciprocating compressors also are used less frequently as primary compressors than they were in the past. Their disadvantages include their close clearances and the pulsating outlet flow of gas. Their main applications now are as interstage boosters in liquefaction systems and as tail/vent gas compressors.

About one-half of the chlorine produced is used as the dry gas and transported directly to the consuming process. The rest is liquefied, stored, and transferred or shipped. Liquefaction usually involves the indirect contact of the compressed gas with a boiling refrigerant. Process conditions are chosen to optimize the total energy consumption of compression of the process gas and compression of the refrigerant (80). Because of the presence of noncondensible gases in the chlorine, complete liquefaction is not possible. These noncondensibles include oxygen formed in the cells, which is the major source of current inefficiency, and carbon dioxide, which results from the decomposition of residual carbonate introduced in the brine purification plant. Air also enters the gas from compressor seals, equipment and pipeline purging, venting of returned shipping containers, and leakage into those parts of the process that are under vacuum.

Any hydrogen present in the chlorine gas as produced is concentrated in the residual gas from liquefaction. Hydrogen is explosive in mixtures with chlorine (see Section 3). The lower explosion limit is very nearly the same as in the case of hydrogen in air, and furthermore the minimum ignition energy is lower in chlorine mixtures. Some plants use liquefiers designed to reduce the probability of explosion and also to contain the energy if an explosion occurs. More often, the process includes dilution of the gas with dry air to keep the hydrogen concentration out of the explosive range. This dilution adds to the noncondensible load and makes liquefaction more difficult. One of the advantages of membrane cells is the lower hydrogen content of the chlorine produced. This reduces the amount of diluent required, or even eliminates the need altogether.

The residual gas from liquefaction is referred to as “tail gas.” This can be combined with chlorine-containing gas from plant evacuation systems and with that from returned shipping containers. Methods of recovery of the chlorine value include the manufacture of certain by-products and the absorption of the chlorine in a solvent from which it later is stripped (81). The latter process relied on carbon tetrachloride, whose use is being phased out under the Montreal Protocol. Several recovery units have accordingly been shut down, and enhanced liquefaction under more severe conditions is becoming more common. This reduces the chlorine content in the tail gas to a point at which it can be utilized as one of the by-products listed in the next paragraph or simply destroyed by absorption in alkaline solution.

Manufactured by-products include hydrogen chloride, formed by controlled combustion of chlorine with a slight excess of hydrogen; various forms of bleach, formed by absorption of chlorine in an alkaline material such as caustic soda or lime; and ferric chloride, formed by the reaction of chlorine or HCl with metallic iron and the further oxidation by chlorine of ferrous chloride to the ferric state.

Hydrogen Processing. The hydrogen produced in all electrolytic chlor-alkali processes is relatively pure (>99.9%) and requires only cooling to remove water along with entrained salt and caustic. The heat is often recovered into the brine system. The hydrogen is compressed using water-sealed liquid-ring pumps, Roots-type blowers or reciprocating compressors. It is desirable, although not always possible, that the entire system from the electrolyzers to the compressor suction is under positive pressure to avoid contamination with air, which could form an explosive mixture. Some uses of hydrogen require additional removal of traces of oxygen. This is accomplished by combination of the oxygen with some of the hydrogen over a platinum catalyst. The hydrogen produced in mercury cells is also contaminated with mercury, which must be removed before using the gas. Cooling removes most of the water in the gas, along with a preponderance of the mercury. Final purification is by scrubbing with an oxidizing solution in which the metal is converted to the more soluble mercuric form, or by adsorption on activated carbon. The carbon usually contains an additive such as sulfur to improve the retention of mercury.

The hydrogen can be used for organic hydrogenation, catalytic reductions, and ammonia or methanol synthesis. It can also be used to provide a reducing atmosphere in some applications or burned with chlorine to produce high quality HCl. The HCl is produced in a high temperature burner and then usually cooled and absorbed in chemically resistant graphite equipment to produce 30–38% acid. Some of this acid goes for sale, and some is used within the chlor-alkali plant to acidify cell-feed brine, to regenerate ion-exchange resins, or to assist in the dechlorination of depleted brine and the water condensed from chlorine gas.

Much of the electrical energy consumed in a cell is associated with the production of hydrogen, and so the gas represents a significant amount of energy. Collection of hydrogen for combustion to provide thermal energy, such as in the production of steam, is a very common practice. Developing technologies may offer more effective means of recovery of the energy in the gas. One such technology is the fuel cell, in which hydrogen and oxygen both are consumed in an electrochemical cell to produce water and energy as direct-current electricity.

Sodium Hydroxide Processing. Coproduct sodium hydroxide is usually sold and shipped as a 50% solution. A 73% solution and the anhydrous material are also marketed. The solutions produced by the various types of cell differ markedly, and the purity of the final product and the energy required to concentrate the cell product to 50% are major differentiators among the three technologies. Diaphragm cells produce a relatively weak liquor of ~10–12% NaOH. Impurities that enter with the treated brine, such as sodium sulfate, and impurities generated in the cells, such as sodium chlorate, accompany the caustic. The unconverted NaCl, in concentrations of 13–16%, also is in the liquor. Evaporation of this mixture toward 50% NaOH causes it to become supersaturated in NaCl, and most of the salt drops out of solution. This salt must be removed, usually by centrifuging, and returned to the brine plant for reuse. Cooling of the solution then rejects more NaCl, which is removed by filtration or centrifuging.

The solubility of NaCl in the cooled solution still is 1% or more, and this salt content is the distinguishing characteristic of diaphragm-cell 50% caustic soda.

The capital and operating costs of the evaporation plant are major factors in diaphragm-cell economics. The relatively low quality of the product makes it unsuited for certain applications, and the products of the other types of cell often are sold at a premium as “rayon grade” or “membrane-cell” grade. Because of the energy consumed in evaporation and the resulting higher heat/power ratio, most large diaphragm-cell plants have associated cogeneration facilities.

Mercury-cell caustic from the decomposers is already 50%, and only filtration to remove mercury droplets is required. The purity of the solution is quite high, and no evaporation is required. Membrane cells produce NaOH at different strengths, depending on the type of membrane used. Plants that sell NaOH usually produce a solution in the 30–40% range. Evaporation is much less expensive than in diaphragm-cell plants, with much lower evaporative loads and no need for salt recovery and handling.

Nickel is the standard material of construction for NaOH evaporators. Multiple-effect units are a universal choice in all but the smallest plants. Membrane-cell plants use double- or triple-effect evaporators. With the high evaporative load associated with the diaphragm-cell process, quadruple-effect systems often are justified. When liquor temperatures in the last effect are sufficiently low, stainless steel is sometimes used in place of nickel.

4.6. Other Chlorine Production Processes.

Electrolytic production of chlorine and NaOH from NaCl accounts for a preponderance of the chlorine produced. Other commercial processes are in operation, and several other processes exist that are no longer practiced commercially.

Chlorine from Potassium Hydroxide Manufacture. Mercury and membrane cells can produce KOH instead of NaOH if KCl is used as the feedstock. Chlorine and hydrogen again are coproducts. The combined nameplate capacity for KOH (caustic potash) in 2001 is about 1.7 MM t/year. Yearly production in 2001 was about 1.4 MM tons. The projected growth rate of 4–5% over the next 5 years (82) will strain the capacity by the end of that interval. The steps involved in the process are identical to those described above, but there are some different characteristics. Potassium chloride is more soluble than NaCl, but the concentrations used around the cells are about the same. Control of the feed brine concentration is therefore more of an issue. Mercury cells are generally more sensitive to trace metals in the brine (83). In membrane cells, much less water is transported through the membranes with potassium ions. The resulting change in the water balance requires more flow on both sides of the cell in order to maintain a given set of operating concentrations.

Chlorine from HCl. Reflecting the low cost, bulk chemical status of the two products, HCl, which otherwise is often made from chlorine, can sometimes be economically converted back to chlorine. There are two fundamentally different approaches, electrolysis and oxidation.

Electrolysis of HCl. Electrolytic decomposition of aqueous HCl to generate chlorine and hydrogen follows the overall reaction:

$$2\,HCl \rightarrow H_2 + Cl_2 \qquad (19)$$

There are a number of these operations around the world, but only one in the United States, operated by Bayer at Baytown, Texas. Installed capacity is >1000 tons/day of chlorine. The typical electrolyzer as provided by Uhde employs graphite electrodes and a PVC or PVC/PVDF diaphragm. The arrangement is bipolar, with one side of an electrode serving as anode and the other as cathode. The assembly resembles a filter press. The effective electrode area is 2.5 m^2, and the current density is 4–5 kA/m^2. The lower figure results in a cell potential of ~1.9 V, corresponding to 1400–1500 kWh/ton of chlorine. The voltage is considerably lower than that in a brine electrolyzer, and oxygen generation is not a problem. This results in much slower deterioration of the electrodes than was experienced in older chlor-alkali cells with graphite anodes.

HCl is the electrolyte on both sides of the cell. The anolyte contains dissolved chlorine. Some of this diffuses through the diaphragm and is reduced at the cathode. This results in a loss of 2–2.5% in current efficiency. A pressure differential between anolyte and catholyte prevents backflow of hydrogen.

The acid strength in a cell is ~17%, with feed at 21–22%. Depleted acid must be reconcentrated for recycle. Most plants are interested in recovery of the chlorine value of HCl because it is a by-product of a chlorination or phosgenation process. Accordingly, the HCl is available in a gas stream. The weak acid then serves as an absorbent, producing 28–30% acid. This is blended with circulating electrolyte to maintain the desired cell feed concentration. Absorption in boiling HCl helps to dissipate the heat of absorption and reject any organics present in the gas.

Chlorine processing is much the same as in the standard electrolytic process. The water content is lower than it is in chlorine generated from NaCl or KCl brine. This fact reduces the demand on the cooling process. Two-stage cooling with chilled water on the second stage still is practiced, and this has the additional advantage of removing nearly all the vaporized HCl from the gas. The hydrogen gas from the cells is saturated with water vapor and HCl, and it also contains some chlorine. First, it is cooled by direct contact with dilute acid. This keeps the bulk of the HCl within the process. A second tower scrubs the gas with a caustic solution to remove residual HCl and chlorine. Another caustic tower can serve as a safety measure in case of breakthrough from the second tower.

These cells can also be fitted with ion-exchange membranes (84). The operating voltage is ~300 mV lower. The lower permeability of membranes also improves the product purity to ~99.5% for both chlorine and hydrogen. The lack of most of the contaminants that are responsible for membrane deterioration in chlor-alkali electrolysis means that membrane life should be longer in this process.

Another development not yet in commercial practice is the electrolysis of anhydrous HCl to form dry chlorine (85). This depends on a cation-exchange membrane to transfer protons from the anode to the cathode side, where water is added to maintain the water content of the membrane and to carry away any HCl that penetrates the membrane.

Other electrolytic processes use metal chlorides to catalyze the process. None is commercial today, but the metals used in the past include nickel, copper, and manganese. The typical process is cyclic, with electrolysis of the chloride producing chlorine and the metal:

$$MCl_2 \rightarrow M + Cl_2 \tag{20}$$

The metal then reacts with HCl to regenerate the chloride:

$$M + 2\,HCl \rightarrow MCl_2 + H_2 \tag{21}$$

The overall reaction is the same as equation 19.

Chemical Oxidation of HCl. Chlorine can also be produced from HCl by the following equilibrium reaction:

$$4\,HCl + O_2 \leftrightarrow Cl_2 + 2\,H_2O \tag{22}$$

Air or oxygen can be used as the oxidizing agent. This reaction is the basis for the Deacon process, which was the first continuous catalytic process carried out on large scale. It was the major source of chlorine before development of the electrolytic route.

The fundamental problem with the Deacon process is the inability to achieve very high degrees of conversion of the HCl. Reactor gas is a high temperature mixture of HCl, water, chlorine, and oxygen and so is very corrosive. When the oxidant is air, there are also large quantities of nitrogen, which make separations more difficult. At the reaction temperatures used, there is also some volatilization of the metal catalyst.

Two other processes used commercially in recent years but no longer in operation are the Shell process (86) and the Kellogg process (87,88). The Shell process carries out reaction 22 in the presence of cupric and other chlorides on a silicate carrier. It operated at 60–70% conversion in the range 430–475°C. The Kellogg process used ~1% nitrosylsulfuric acid [7782-78-7] catalyst and a dissimilar material containing a clay desiccant with a reversible water content of ~0.5 wt% and a crystalline structure stable to at least 760°C. It absorbs water as it forms, shifting the equilibrium of equation 22 to the right. The basic reaction was carried out in a fluidized bed in which the solids ran countercurrent to the gaseous reactants at a temperature of 400–500°C and pressures of 300–1200 kPa (3–12 atm). The process fluids are extremely corrosive, and tantalum-lined or plated equipment and piping were used.

Another variation on HCl oxidation is Mitsui Toatsu's MT Chlor process. This is essentially a Deacon reaction carried out in a fluidized bed, using a chromium oxide catalyst.

More recently, a new "carrier catalyst" process has been studied in which the basic Deacon reaction is carried out in stages in fluidized beds (89,90). The active catalyst is copper chloride on an inert support. Two-stage operation improves the achievable conversion of HCl to chlorine. The catalyst, in different states of oxidation, is transferred back and forth between the beds. The first stage is the "chlorination" reactor in which HCl reacts with a partly oxidized form of the catalyst to produce copper chloride and water.

$$4\,HCl + 2\,CuO \rightarrow 2\,CuCl_2 + 2\,H_2O \tag{23}$$

In the second (oxidation) stage, the chlorinated catalyst, by reaction with oxygen, reverts to its oxidized form and releases chlorine gas:

$$2\,\mathrm{CuCl_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{CuO} + 2\,\mathrm{Cl_2} \tag{24}$$

The sum of the two reactions is the same as equation 22 with the catalyst in effect "carrying" chlorine from one stage to the other. Running the two stages at different temperatures, in particular with a lower temperature in the chlorination reactor, allows conversions higher than typical Deacon process equilibrium to be obtained. This process has been operated on a small scale in a pilot plant in Spain. A new plant was just announced, using a process developed by Sumitomo.

Chlorine from the Magnesium Process. Magnesium is produced by the fused salt electrolysis of $MgCl_2$ (see MAGNESIUM AND MAGNESIUM ALLOYS). The largest magnesium plant in the United States, that of Dow Chemical at Freeport, Texas, shut-down in 1998, used calcium–magnesium carbonate as a raw material, and the chlorine was recycled within the process. The Rowley, Utah, plant of AMAX Magnesium Corporation produces the metal directly from purified $MgCl_2$ recovered from the Great Salt Lake.

Chlorine from the Titanium Process. Electrolysis of magnesium chloride is a step in the production of titanium. Titanium metal is produced by the reaction of titanium tetrachloride with magnesium (see TITANIUM AND TITANIUM ALLOYS). The magnesium chloride formed in this reaction is electrolyzed, as in the preparation of magnesium. Usually, the chlorine is recycled in the production of $TiCl_4$ from the titanium dioxide ore rutile [1317-80-2]. A variation is the purchase of $TiCl_4$ [7550-45-0] and the sale of the chlorine generated by $MgCl_2$ electrolysis.

4.7. Energy Requirements. The minimum amount of electrical energy required for producing 1 ECU (electrochemical unit), constituting 1 mol of chlorine and 2 mol of caustic is 5.75×10^6 Btu or 1686 kWh for 1 ton of chlorine and 1.1 tons of caustic soda. The corresponding value for 1 short ton of chlorine and 1.1 tons of sodium hydroxide is 5.23×10^6 Btu or 1534 kWh. The total energy consumed in the year 1999 by the chlor-alkali industry is $\sim 48 \times 10^9$ kWh to produce 14.14 MM short tons of chlorine, representing 1.2% of the total annual production of 3800×10^9 kWh (91–93).

Electrolytic Decomposition of Sodium Chloride. Electrolysis of aqueous solutions of sodium chloride [7647-14-5], NaCl (or KCl), commonly called brine, simultaneously generates chlorine and caustic soda (or potash), following the overall chemical reactions:

$$2\,\mathrm{NaCl} + 2\,\mathrm{H_2O} \xrightarrow{\text{electrical energy}} 2\,\mathrm{NaOH} + \mathrm{H_2} + \mathrm{Cl_2} \tag{25}$$

$$2\,\mathrm{KCl} + 2\,\mathrm{H_2O} \xrightarrow{\text{electrical energy}} 2\,\mathrm{KOH} + \mathrm{H_2} + \mathrm{Cl_2} \tag{26}$$

Reactions 25 and 26 have a positive free energy change of 422.2 kJ (or 100.95 kcal)/ mol of chlorine at 25^0C and 417.8 kJ (or 99.90 kcal), respectively, at 95°C. Therefore, energy has to be provided in the form of dc electricity to force the reaction to proceed in the forward direction. The amount of electrical energy required depends on the amount of the product needed and the electrolytic cell parameters, current density and cell voltage—the latter being dictated by the nature of the anode and cathode material, the separator, the interelectrode gap and the cell design.

Production of chlorine and caustic from brine is accomplished in three types of electrolytic cells: the diaphragm, the membrane, and the mercury cell. The distinguishing characteristic of these cells is the manner in which the electrolytic products are prevented from mixing with each other.

The primary electrochemical reactions during the electrolysis of brine are the discharge of the chloride ion at the anode to form chlorine,

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \tag{27}$$

and the generation of hydrogen [1333-74-0], and hydroxide ions, OH^-, at the cathode.

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{28}$$

Chlorine is generated at the anode in all the three types of electrolytic cells. The cathodic reaction in diaphragm and membrane cells is the electrolysis of water to generate hydrogen as described by equation 28, whereas the cathodic process in mercury cells is the discharge of sodium ion, Na^+, to form sodium amalgam containing 0.2–0.3% sodium.

$$Na^+ + Hg + e^- \rightarrow Na(Hg) \tag{29}$$

This amalgam is subsequently reacted with water in denuders or decomposers to generate hydrogen and caustic.

$$2\,Na(Hg) + 2\,H_2O \rightarrow 2\,NaOH + 2\,(Hg) + H_2 \tag{30}$$

Separation of the anode and cathode products in diaphragm cells is realized using asbestos [1332-21-4], polymer-modified asbestos composite, or non-asbestos material deposited on a foraminous cathode. In membrane cells, the separator is a cation-exchange membrane. Mercury cells require no diaphragm or membrane, the mercury itself acting as a separator.

The catholyte from diaphragm cells typically contains 9–12% caustic soda and 14–16% salt. This cell liquor is concentrated to 50% NaOH in a series of evaporation steps involving three or four stages. Membrane cells produce 30–35% NaOH that is evaporated in two or three stages to produce 50% caustic soda. A 50% caustic soda containing very little salt is made directly in the mercury cell process by reacting the sodium amalgam with water in the decomposers.

Energy Consumption and its Components. Faraday's law states that 96,487 C (1 C = 1 amp s) are required, for a single electron process, to produce 1 g equiv weight of the electrochemical reaction product. This relationship determines the minimum coulombic requirements for chlorine and caustic production, in units of kilo ampere hours per metric ton of Cl_2 or NaOH.

$$\text{For } Cl_2 \ \frac{96,487\times 1000}{60\times 60\times 35.45}=756.2\,\text{kA h/t}$$

$$\text{For NaOH } \frac{96,487\times 1000}{60\times 60\times 40.00}=670.3\,\text{kA h/t}$$

$$\text{For KOH } \frac{96,487\times 1000}{60\times 60\times 56.09}=477.8\,\text{kA h/t}$$

The current efficiency of an electrolytic process (η_{current}) is the ratio of the amount of material produced to the theoretically expected quantity.

Energy consumption, expressed in terms of kilowatt hours per ton of Cl_2 (E_{Cl2}) or of NaOH (E_{NaOH}), is the popular terminology in the chlor-alkali industry to describe and evaluate cell performance. Calculation of this value requires information related to the operating cell voltage, $V_{\text{cell}} = V_{\text{Total}}/N$, where N = number of cell elements, the current efficiency, η_{current}, and the efficiency of the rectifier used to convert ac power to dc power, $\eta_{\text{rectifier}}$. The energy consumption for producing a metric ton of Cl_2, in units of ac kwh per ton of product is :

$$E_{Cl_2}=\frac{756.2\,V_{\text{cell}}}{\eta_{\text{current}}\eta_{\text{rectifier}}}$$

and that for a ton of NaOH is

$$E_{\text{NaOH}}=\frac{670.3\,V_{\text{cell}}}{\eta_{\text{current}}\eta_{\text{rectifier}}}$$

For KOH, the corresponding value is

$$E_{\text{KOH}}=\frac{477.8\,V_{\text{cell}}}{\eta_{\text{current}}\eta_{\text{rectifier}}}$$

The minimum energy required to produce chlorine, hydrogen and caustic from salt is the same (ie, 1686.32 kWh/ton of chlorine) for all three cell technologies. However, the actual energy consumed is much higher than the minimum. The energy consumed in the mercury-cell process is the greatest because the combined voltages required by reactions 29 and 30 are higher those encountered in the diaphragm- or membrane-cell process.

Electrolysis of brine is endothermic. The overall heat of the reaction is 446.68 kJ or (106.76 kcal)/mol of chlorine and hence the thermoneutral voltage, ie, the voltage at which heat is neither required by the system nor lost by the system to the surroundings, would therefore be 2.31 V. In practice, however, chlor-alkali cells operate in the range of 3.0–3.5 V, at an average chlorine efficiency (CE) of 95%, resulting in heat generation (Q) to the extent of 3960 kJ/kg (1710 Btu/lb) of Cl_2 for a voltage of 3.5 V as:

$$Q=\left[\left(\frac{100}{\text{CE}}\right)(46.05\,\text{V})\right]-\Delta H$$

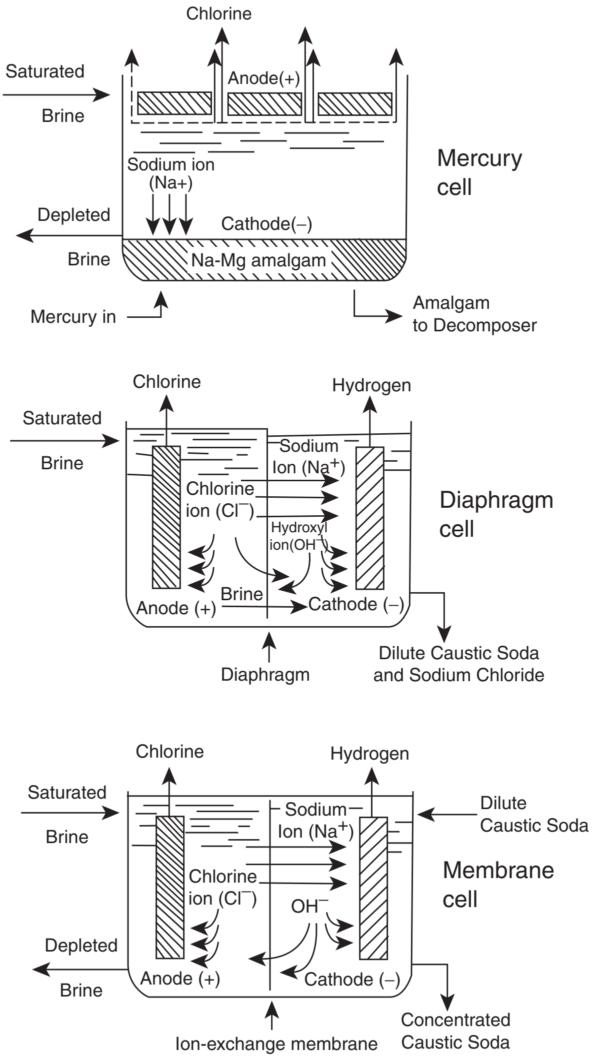


Fig. 28. Chlorine electrolysis cells.

Heat produced in these cells operating at voltages >2.31 V is generally removed by water evaporation and radiation losses. Figure 28 illustrates the basic principles of the three cell processes and Table 8 summarizes the differences in the cell technologies and their performance.

The values of energy consumption presented in Table 9 are not optimal for the given technology, since the actual value depends on the current density, cell voltage, and current efficiency, which are affected by the process variables. Similarly, the energy for evaporation varies with the type of the evaporator system used. In the case of membrane cells, the energy requirements would be 15–25% lower than those for diaphragm cells—the major savings resulting from caustic evaporation. Thus, the energy needed to concentrate 33% NaOH to

Table 8. **Comparison of Diaphragm, Membrane, and Mercury Cells**

Component	Mercury cell	Diaphragm cell	Membrane cell
anode	$RuO_2 + TiO_2$ coating on Ti substrate	$RuO_2 + TiO_2 + SnO_2$ on Ti substrate	$RuO_2 + IrO_2 + TiO_2$ coating on Ti substrate
cathode	mercury on steel	steel (or steel coated with activated nickel)	nickel coated with high area nickel based or noble metal based coatings
separator	none	asbestos, polymer-modified asbestos, or nonasbestos diaphragm	ion-exchange membrane
cathode product	sodium amalgam	10–12% NaOH + 15–17% NaCl + 0.04–0.05% $NaClO_3$, and H_2	30–33% NaOH + <0.01% NaOH and H_2
decomposer product	50% NaOH and H_2	none	none
evaporator product	none	50% NaOH with ~1.1% salt and 0.1–0.2% $NaClO_3$	50% NaOH with ~0.01% salt
steam consumption	none	1500–2300 kg/t NaOH	450–550 kg/t NaOH
cell voltage, V	4–5	3–4	2.8–3.3
current density, kA/m^2 energy consumption (kWh/ton of Cl_2)	7–10	0.5–3	2–6
electricity for electrolysis	3200–3600	2800–3000	1950–2220[b]
steam for [a] caustic evaporation	0	600–800	200–350[c]
total	*3200–3600*	*3400–3800*	*2150–2570*

[a] 1 ton of steam = 400 kWh.

[b] Load: 3–6 kA/m^2.

[c] MP steam(10 bar a, 200°C) double effect evaporator.

Table 9. **Thermodynamic Decomposition Voltage of Chlor-Alkali Cells**

	Diaphragm/Membrane cell (at 90°C)	Mercury cell (at 80°C)
anode reaction	$2Cl^- \rightarrow Cl_2 + 2e^-$	$2Cl^- \rightarrow Cl_2 + 2e^-$
anode potential, E^0, V	1.36	1.36
cathode reaction	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$Na^+ + e^- \rightarrow Na\,(amalgam)$
cathode potential, E^0, V	− 0.89	− 1.80
overall reaction	$2H_2O + 2Cl^- \rightarrow Cl_2 + 2OH^- + H_2$	$2H_2O + 2Cl^{Hg}\,Cl_2 + 2Na(Hg)$
cell potential, E^0, V	2.25	3.15

50% caustic can vary from 720 kWh/ton of caustic to 314 kWh/ton, depending on whether a single effect or a triple effect is used for caustic concentration.

There are several inefficiencies arising from parasitic reactions occurring at the electrodes and in the bulk, which are described below. The two parasitic reactions offsetting anode efficiency are (1) cogeneration of oxygen [7782-44-7], from the anodic discharge of water,

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{31}$$

and (2) electrochemical oxidation of hypochlorite ion, OCl^-, to chlorate, $ClO_3{}^-$:

$$6\,OCl^- + 3\,H_2O \rightarrow 2\,ClO_3^- + 4\,Cl^- + 6\,H^+ + 3/2\,O_2 + 6\,e^- \tag{32}$$

The amount of oxygen generated from these reactions depends on the nature of the anode material and the pH of the medium. The current efficiency for oxygen is generally 1–3% when using commercial metal anodes.

At the cathode, water molecules are discharged to form gaseous hydrogen and hydroxide ions, OH^-. Some of the caustic generated in the cathode compartment back-migrates to the anode compartment and reacts with dissolved chlorine, $Cl_{2(aq)}$, to form chlorate as follows:

$$Cl_{2(aq)} + OH^- \rightarrow HOCl + Cl^- \tag{33}$$

$$HOCl + OH^- \leftrightarrow H_2O + OCl^- \tag{34}$$

$$2\,HOCl + OCl^- \rightarrow ClO_3^- + 2\,H^+ + 2\,Cl^- \tag{35}$$

There are two reactions that influence the cathodic efficiency, viz, the reduction of OCl^- and $ClO_3{}^-$

$$OCl^- + H_2O + 2\,e^- \rightarrow Cl^- + 2\,OH^- \tag{36}$$

$$ClO_3^- + 3\,H_2O + 6\,e^- \rightarrow Cl^- + 6\,OH^- \tag{37}$$

Although these reactions are thermodynamically possible, they are not kinetically significant under normal operating conditions. Hence, the cathodic efficiency is usually high (>95%) in diaphragm and membrane cells. In mercury cells, the cathodic inefficiency arises from the discharge of H_2 at the cathode as a result of the impurities in the brine. Reactions contributing to anodic inefficiency in mercury cells are the same as in diaphragm or membrane cells.

Current Efficiency. Current efficiency for caustic production in mercury, diaphragm and membrane cells can be determined by collecting a known amount of caustic over a given time, and from a knowledge of the number of coulombs of electricity passed during that period. The ratio of the amount of caustic collected to that expected from Faraday's law provides the magnitude of the current efficiency. An alternative method involves analysis of the gases evolved during electrolysis and the anolyte composition.

The chlorine and caustic current efficiency expressions (94,95), based on rigorous material balance calculations, for all three cell technologies are shown in equations 38–43. The symbol eta denotes the current efficiency for the product in the subscript and the technology in the superscript, Hg for mercury cells, *d* for diaphragm cells, and *m* for membrane cells. Superscripts *f* and *d* refer to the feed and depleted streams respectively.

Membrane Cells

$$\eta^{m}_{\mathrm{Cl_2}} = \frac{1 - (2\mathrm{F/I})p(X\mathrm{Cl}_2^d - \mathrm{Cl}_2^f)}{C - 2Y\mathrm{Cl}_2^d} \tag{38}$$

$$\eta^{m}_{\mathrm{NaOH}} = \frac{1 - (\mathrm{F/I})p\left[2(1-C)(L\mathrm{Cl}_2^d - \mathrm{Cl}_2^f) + C(L\mathrm{OH}^d - \mathrm{OH}^f)\right]}{C - M\left[2(1-C)\mathrm{Cl}_2^d + C\mathrm{OH}^d\right]} \tag{39}$$

where $F =$ Faraday; $I =$ current (amps); $p =$ feed brine flow rate(L/sc):

$$C = 1 + 2(\%\mathrm{O_2} + \%\mathrm{Cl_2});\quad X = \mathrm{Cl}^f/\mathrm{Cl}^d;\quad Y = 1/\mathrm{Cl}^d :$$

$$\mathrm{Cl}_2^f = \mathrm{Cl}^f_{\mathrm{Cl_2}} + C^f_{\mathrm{HOCl}} + C^f_{\mathrm{NaOCl}} + 3C^f_{\mathrm{NaClO_3}}$$

$$\mathrm{Cl}_2^d = \mathrm{Cl}^d_{\mathrm{Cl_2}} + C^d_{\mathrm{HOCl}} + C^d_{\mathrm{NaOCl}} + 3C^d_{\mathrm{NaClO_3}}$$

$$\begin{aligned}
\mathrm{Cl}^f &= C^f_{\mathrm{NaCl}} + 2C^f_{\mathrm{Cl_2}} + C^f_{\mathrm{HOCl}} + C^f_{\mathrm{NaOCl}} + C^f_{\mathrm{NaClO_3}} + C^f_{\mathrm{HCl}}\\
\mathrm{Cl}^d &= C^d_{\mathrm{NaCl}} + 2C^d_{\mathrm{Cl_2}} + C^d_{\mathrm{HOCl}} + C^d_{\mathrm{NaOCl}} + C^d_{\mathrm{NaClO_3}} + C^d_{\mathrm{HCl}}\\
\mathrm{OH}^f &= C^f_{\mathrm{HOCl}} + 2C^f_{\mathrm{NaOCl}} + 6C^f_{\mathrm{NaClO_3}} + 2C^f_{\mathrm{Na_2CO_3}} + C^f_{\mathrm{NaHCO_3}}\\
&\quad + C^f_{\mathrm{NaOH}} - C^f_{\mathrm{HCl}} - C^f_{\mathrm{NaHSO_4}}\\
\mathrm{OH}^d &= C^d_{\mathrm{HOCl}} + 2C^d_{\mathrm{NaOCl}}
\end{aligned}$$

The C values in the above equation refer to concentrations of the species in the subscript, the superscript representing the feed (f) or depleted (d) stream.

Diaphragm Cells.

$$\eta^{d}_{\mathrm{Cl_2}} = \frac{\eta^d_{\mathrm{H_2}} + \frac{\mathrm{F}}{I}p\left\{6C^f_{\mathrm{NaClO_3}} + C \times G\right\}}{C + 6(C^d_{\mathrm{NaClO_3}}/C^d_{\mathrm{NaOH}})} \tag{40}$$

$$\eta^{d}_{\mathrm{NaOH}} = \frac{\eta^d_{H_2} + \frac{6F}{I}p\left\{C^f_{\mathrm{NaClO_3}} - \left(\frac{C^d_{\mathrm{NaClO_3}}}{C^d_{\mathrm{NaOH}}}\right)G\right\}}{C + 6(C^d_{\mathrm{NaClO_3}}/C^d_{\mathrm{NaOH}})} \tag{41}$$

where

$$G = C^f_{\mathrm{NaOH}} + 2C^f_{\mathrm{Na_2CO_3}} + C^f_{\mathrm{NaHCO_3}} - C^f_{\mathrm{HCl}} - C^f_{\mathrm{NaHSO_4}}$$

$$\eta^d_{\mathrm{H_2}} = 1 - 2(C^a_{\mathrm{av.Cl_2}}/C^d_{\mathrm{NaOH}})$$

$C^a_{\mathrm{av.Cl_2}} =$ concentration of available chlorine in the anolyte

Mercury Cells

$$\eta_{\mathrm{Cl_2}}^{\mathrm{Hg}} = \frac{1}{C - \left(\frac{6\Delta C_{\mathrm{NaClO_3}} + 2\Delta C_{\mathrm{Av.Cl_2}}}{\Delta C_{\mathrm{Cl}}}\right)} \tag{42}$$

$$\eta_{\mathrm{NaOH}}^{\mathrm{Hg}} = \left\{\frac{\Delta C_{\mathrm{NaCl}} + \Delta C_{\mathrm{NaClO_3}} + \Delta C_{\mathrm{NaOCl}}}{\Delta C_{\mathrm{Cl}}}\right\}\eta_{\mathrm{Cl_2}}^{\mathrm{Hg}} \tag{43}$$

where,

$$\Delta C_{\mathrm{NaClO_3}} = C_{\mathrm{NaClO_3}}^{f} - C_{\mathrm{NaCl}}^{d}$$

$$\Delta C_{\mathrm{av.Cl_2}} = C_{\mathrm{av.Cl_2}}^{f} - C_{\mathrm{av.Cl_2}}^{d}$$

$$\Delta C_{\mathrm{NaCl}} = C_{\mathrm{NaCl}}^{f} - C_{\mathrm{NaClO_3}}^{d}$$

$$\Delta C_{\mathrm{NaOCl}} = C_{\mathrm{NaOCl}}^{f} - C_{\mathrm{NaOCl}}^{d}$$

$$\Delta C_{\mathrm{Cl}} = \left(C_{\mathrm{NaCl}}^{f} - C_{\mathrm{NaClO_3}}^{f} + C_{\mathrm{Cl_2}}^{f} + C_{\mathrm{av.Cl_2}}^{f} + C_{\mathrm{HCl}}^{f}\right) - \left(C_{\mathrm{NaCl}}^{d} - C_{\mathrm{NaClO_3}}^{d} + C_{\mathrm{Cl_2}}^{d} + C_{\mathrm{av.Cl_2}}^{d} + C_{\mathrm{HCl}}^{d}\right)$$

$C_{\mathrm{av.Cl2}}$ = concentration of available chlorine that includes dissolved chlorine, HOCl and NaOCl in the given stream.

Equation 43 assumes that all the sodium amalgam is decomposed to form caustic in the decomposer. Otherwise, appropriate corrections are needed to account for the incomplete decomposition of the sodium amalgam.

The disparity in the chlorine and caustic efficiency values are a result of the alkalinity or acidity in the feed brine as described by equation 44

$$\eta_{\mathrm{NaOH}} - \eta_{\mathrm{Cl_2}} = \frac{\mathrm{F}}{I}\Delta\{J_{\mathrm{NaOH}} + 2J_{\mathrm{Na_2CO_3}} + J_{\mathrm{NaHCO_3}} - J_{\mathrm{HOCl}} - J_{\mathrm{HCl}} - 2J_{\mathrm{Cl_2}}\} \tag{44}$$

where J values represent the difference in the mass flow rates of the species in the subscript between the feed and depleted brine streams.

Equation 40 is the proper material balance expression for calculating the chlorine efficiency of diaphragm cells. However, many approximate versions are practiced (91), the one closest to the material balance expression (eq. 40) being the "six equation":

$$\eta_{\mathrm{Cl_2}} = \left[\frac{100}{1 + 2(\%\mathrm{O_2} + \%\mathrm{Cl_2}) + 6C_{\mathrm{NaClO_3}}(\text{cell liquor})/C_{\mathrm{NaOH}}}\right] \tag{45}$$

Current efficiency values based on the "six equation" are higher by ~1.0% than those from equation 40.

Cell Voltage and Its Components: The cell voltage, E, is composed of various terms as

$$E = E^0 + |\text{Overvoltages(anodic and cathodic)}| + \text{ohmic drops} \tag{46}$$

The ohmic drops in the above equation are associated with the electrolyte, the separator, and the hardware.

The minimum voltage required for electrolysis for a given set of cell conditions, such as a temperature of 95°C, is the sum of the cathodic and anodic reversible potentials and is known as the thermodynamic decomposition voltage, E°. The parameter E° is related to the standard free energy change ΔG° for the overall chemical reaction 25 or 26 as

$$\Delta G^0 = -n\mathrm{F}E^0$$

where n refers to the number of electrons involved in the primary electrode reaction and F is the Faraday constant, expressed in ampere-hours equiv. The E° values for all three types of cells are presented in Table 10. The + 0.924 V difference in E° values between diaphragm or membrane and mercury cells arises from the reaction:

$$2\,\mathrm{Na} + 2\,\mathrm{H_2O} \rightarrow 2\,\mathrm{NaOH} + \mathrm{H_2}$$

which takes place outside the electrolytic cells. Although, in principle, this voltage is recoverable, this concept has not yet been commercially demonstrated. The E° value for diaphragm or membrane cells at 95°C is 2.23 V for a caustic concentration of 3.5 *M*. However, the electrolytic cells operate 3.0–3.2 V at current density of 2–3 kA/m^2, not at 2.23 V, because in order to achieve acceptable rates, an additional driving force is required to overcome cell resistances and electrode overvoltages.

Table 10. **Components of Chlor-Alkali Cell Voltages**

	Diaphragm cell[a]	Membrane cell[b]	Mercury cell[c]
Thermodynamic decomposition voltage			
anode	1.32	1.32	1.32
cathode	0.93	0.93	1.83
Overvoltage			
anode	0.03	0.05	0.1
cathode	0.28	0.10	0.4
Ohmic drops			
solution	0.12	0.20[d]	0.15
diaphragm/membrane	0.38	0.44	
anode and contact to base	0.11		
base	0.06	0.03[e]	0.2
Cathode	0.09		
Cell voltage	3.32	3.07	4.0

[a] Voltages given are for Oxy Tech H4 cell operating at 2.3 kA/m^2 (150 kA and 95°C).

[b] Voltages given are for third generation Uhde's single cell element operating at 5.0 kA/m^2 (90°C).

[c] Voltages given are for De Nora 24M2 system operating at 10 kA/m^2 (270 kA and 80°C).

[d] With 1.2-mm gap.

[e] Total structural *IR* drop.

Overvoltage. Overvoltage (η_{ac}) arises from kinetics of the electrode reaction on a given substrate. The magnitude of this value is generally expressed in the form of the Tafel equation:

$$\eta_{ac} = k\log(i/i_0) \tag{49}$$

where k is the slope of the η_{ac} vs log i curve, i is the applied current density, and i_o is the exchange current density of the reaction. The quantity i_o is a measure of the rate of a given reaction, eg, 1 mA/cm^2 for the Cl_2 evolution on dimensionally stable electrodes (DSA). Overvoltage can be lowered by increasing the electrochemically active surface area, which reduces the magnitude of i, or by using materials exhibiting high exchange current density.

Ohmic Drops. Voltage drops across the electrolyte between the electrodes, separator and the hardware constitute a significant portion of the overall cell voltage. The ohmic R drop across the hardware, also called as IR drop, can be calculated from Ohm's law and the relationship:

$$R = \rho l/A \tag{50}$$

where R is the resistance (in Ω) of the conductor of length l with a specific resistance of ρ and cross-sectional area A.

The ohmic drop across the electrolyte and the separator can also be calculated from Ohm's law using a modified expression for the resistance. When gas bubbles evolve at the electrodes, they are dispersed in the electrolyte and the resulting conductivity characteristics of the medium will be different from those of a pure electrolyte. According to Rousar (96), the resistance of the gas-electrolyte mixture R_{mix}, is related to the pure electrolyte, R_{sol}:

$$R_{\text{mix}} = R_{\text{sol}}\,(1 + 1.5\epsilon) \tag{51}$$

where ε is the gas void fraction, defined as the ratio of the volume of the gas to the volume of the gas plus the volume of the electrolyte. The *IR* drop in brine solution is generally ~30–40 mV/mm at 95°C and a current density of 2.32 kA/m^2. Similarly, for calculating the IR drop across the separator, the separator thickness term has to be modified because the distance between the two faces of a separator such as the asbestos diaphragm is not equal to its thickness. The liquid path is tortuous and the area is limited by finite porosity. Thus, the *IR* drop across the separator would be

$$IR_{\text{sep}} = xil\rho \tag{52}$$

where x reflects the tortuosity-to-porosity ratio. Typical values of tortuosity for asbestos diaphragms range from 2.2 to 2.8; porosity varies from 0.7–0.8.

The conductivity of the composite membranes constituting the perfluorsulfonic and perfluorocarboxylic layers is best determined experimentally, although some approximate theoretical descriptions are available (50, 97–99). Its value in the chlor-alkali cell operating environment is in the range of 1.5–2 Ω -cm^2. Note, however, that the membrane manufacturers are constantly striving to develop new compositions to lower the resistance and at the same time achieve better performance and life.

The components of the diaphragm-, membrane-, and mercury-cell voltages presented in Table 10 show that the major components of the cell voltage are the E° term and the ohmic drops.

Direct-Current Electric Power. The operation of a chlor-alkali plant is dependent on the availability of large quantities of dc electric power, which is usually obtained from a high voltage source of alternating current. The lower voltage required for an electrolyzer circuit is produced by step-down transformers. Silicon thyristor rectifiers convert the ac to dc for the electrolysis. A set of rectifiers can supply up to 450 kA. Although these devices can operate at 400 V/device, a peak ac voltage of 1500 V, corresponding to a dc output of 1200 V is not exceeded for safety reasons. Rectifier efficiency ($\eta_{\text{rectifier}}$) is generally ~97.5–98.5%. The harmonics fed back to the supply system as a result of thyristor operation are kept within limit by providing suitable harmonic filters.

Older generation high current rectifier systems based on diodes and transformers with on-load tap changers are now being replaced by new generation rectifier systems using thyristors as the devices. A thyristor rectifier system has following advantages over the diode type:

(*1*) Rapid current regulation due to control by solid-state devices as compared to diode type where the control is by operation of saturable reactors, which are slower in their response.
(*2*) Smooth control of current and voltage.
(*3*) Better overall system efficiency.
(*4*) Compact size and layout.

The thyristor rectifier system, however, generates greater harmonic currents and voltages, and operates at relatively lower power factor. These harmonics can be filtered by providing suitable tuned capacitor banks which also improve the operating power factor of the system.

The unit cost of the dc supply decreases with increasing voltage and amperage (Fig. 29). An electrolytic plant is therefore most economical when as many

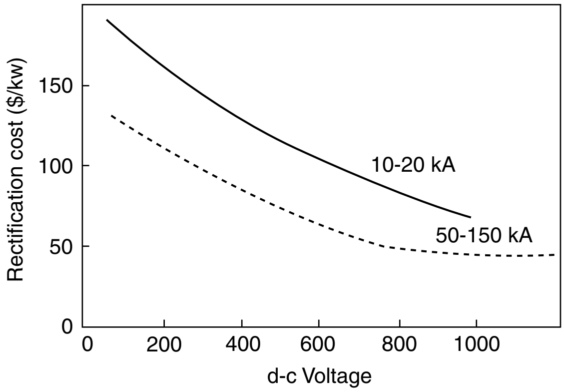


Fig. 29. Variation of rectification costs with voltage (100).

high amperage cells as possible are connected in series. The costs (100) in Figure 29 are for the rectification equipment with optimum medium distribution voltage level delivering ac power to the rectifier-transformer primary. Advances in transformer and rectifier design allow large rectifiers to be connected directly to voltages up to 138 kV. Such a configuration increases the rectification cost by 10–15% while saving plant space, and the cost and energy losses associated with the step-down transformers. These costs were typical for 2001. Various design and performance options result in a variation of ± 15%.

5. Materials of Construction

The choice of construction material for handling chlorine depends on equipment design and process conditions. Dry chlorine, with <50 ppm (w/w) of water, can be handled safely below 120°C in iron, steel, stainless steels, Monel, nickel, copper, brass, bronze, and lead. Silicones, titanium, and materials with high surface areas (eg, steel wool) should be avoided. Titanium ignites spontaneously at ordinary temperatures in dry chlorine; steel reacts at an accelerated rate at temperatures above 120°C, igniting near 250°C (17). The presence of rust or organic substances increases the risk of steel ignition because of the exothermic reactions of these materials with chlorine. Thorough cleaning, degreasing, and drying are essential before commissioning the steel equipment into chlorine service.

With chlorine gas, ordinary carbon steel is safe so long as the temperature is held safely below the ignition temperature. Good practice allows a wide margin to allow for hot spots and to extend the life of the equipment. In the chlorine production process, the only step in which dangerous temperatures normally may occur is compression. Limiting the compression ratio in each stage and cooling the gas before the compressor and between stages keeps the temperature low. In those applications of chlorine that require temperatures above 150°C, materials of construction other than carbon steel must be used.

The atmospheric pressure boiling point of chlorine (−34°C) demands the use of low temperature carbon steels. Because this temperature is possible whenever a higher pressure system is depressurized, most liquid chlorine systems are constructed of these materials. Liquid chlorine usually is stored in vessels made from unalloyed carbon steel or cast steel. Fine grain steel with limited tensile strength is used to facilitate proper welding.

A protective layer of ferric chloride on the metal prevents the reaction of dry chlorine with steel. This layer can be disrupted by excessive temperature (as above), the presence of moisture, or erosion. Accordingly, the velocity of liquid chlorine in piping is limited to 2 m/s. In long-distance transfer lines, a lower limit may be used. Both Euro Chlor (101) and The Chlorine Institute (102) provide specifications for chlorine piping. The latter divides services into six classes, with three different temperature ranges for gas systems and for liquid systems or those systems that may carry liquid. Euro Chlor also has an official procedure for homologation of valves, and various suppliers certify valves to these specifications. Reference 102 directs a reader to specifications for various types of valves.

Wet chlorine gas is handled in fiberglass-reinforced plastics. Special constructions are necessary to achieve optimum performance (103). Rubber-lined steel is suitable for wet chlorine gas up to ~100°C. At low temperature and pressure, PVC, CPVC, and reinforced polyester resins are also used. PTFE, PVDF (polyvinylidene fluoride), and FEP (fluorinated ethylene propylene) are resistant at higher temperatures but suffer from permeability or poorer mechanical properties. Other materials stable in wet chlorine include graphite and glass. Among the metals, titanium is the usual choice for wet-chlorine service. As was the case with steel in dry chlorine, titanium depends on a protective layer (TiO_2) on the metal for its corrosion resistance. Maintenance of this layer requires a minimum water content in the gas (76,78). Tantalum is the most resistive metal over a wide range of conditions. Its limited availability and high price preclude its use in large equipment, but it is quite common in small parts and instrument systems.

Gaskets in both dry gas and liquid chlorine have been made for many years from some form of compressed asbestos. It is an ideal material for the service, but restrictions on the use of asbestos have led to development of alternatives. Both Euro Chlor (104) and The Chlorine Institute (105) have active programs for the evaluation of these alternatives. For wet chlorine gas, rubber or synthetic elastomers are acceptable. PTFE within its serviceable temperature range is resistant to all forms of chlorine. Tantalum, Hastelloy C, PTFE, PVDF, Monel, and nickel are used in thin sections such as diaphragms, membranes, rupture disks, and bellows.

6. Shipment and Storage

There are two basically different approaches to storing chlorine. One is to store it under positive pressure; the other is to refrigerate it and store it essentially at atmospheric pressure. In a producing plant, the former usually is at liquefaction process pressure. The latter is mechanically more complex and requires a compression system for returning vaporized chlorine to the process. It is considered appropriate only for large systems in producers' plants. Pressurized storage tanks require relief and containment systems. It is common to use an empty expansion tank as a receptacle for escaping chlorine. This contains the material released during minor upsets and buffers the flow of gas to a scrubbing system when releases are too large to be completely contained.

The material of construction for atmospheric storage tanks is unalloyed low-temperature carbon steel. These tanks usually are approximately spherical and are contained within a shell. Overcoming differential thermal expansion is an important part of vessel design and fabrication. The annular space contains insulation and is monitored for chlorine leaking from the inner tank. While the temperature of the chlorine under pressurized storage may be above the minimum temperature for conventional steels (−29°C), such low temperatures are encountered whenever pressure is released from a tank. Normal practice therefore is to build these also from low temperature steel. Chlorine Institute Pamphlet 5 summarizes design principles and good practice.

Liquid chlorine has an unusually large coefficient of thermal expansion. The amount stored in a pressurized tank must be limited to allow for this expansion in case the temperature is allowed to rise. A standard practice is to design for a filling density of 1.25 in order to give 5% freeboard at 50°C.

Because stored liquid chlorine frequently represents a plant's hazard with the most serious potential consequences, the trend is to keep storage volumes to a reasonable minimum.

Chlorine loading and unloading are usually by one of two methods, pumping or pressurization with a dry gas. Pumps in large-scale storage systems usually are of the submerged type. This eliminates suction piping and the need for bottom or side connections to the storage tanks. Excess flow valves prevent release of chlorine in case of downstream maloperation or piping failure. Canned pumps are an alternative and are popular in Europe. Pressurization is mechanically simpler but creates the need for disposal of the padding gas, mixed with residual chlorine.

Chlorine is transported in cylinders and ISO (International Standards Organization) containers and by rail and road tankers. It is classified as a nonflammable compressed gas. U.S. Department of Transportation regulations call for a green label. Repackagers of chlorine supply it in small cylinders containing 45.4 or 68 kg. They also, along with some producers, supply ton lots in cylinders. These are pressurized and protected with fusible-plug relief devices. Quantities between 15 and 90 short tons are transported in tankers with covered manholes fitted with special angle valves. In the United States, shipping containers are fitted with special relief devices comprising a diaphragm-protected conventional relief valve mounted above a breaking-pin assembly. Thinking on the matter of relief of transport containers is divided, and in Europe chlorine is shipped without relief devices (106).

7. Economic Aspects

The choice of technology, the associated capital and operating costs for a chlor-alkali plant are strongly dependent on the local energy and transportation costs, as well as environmental constraints. The primary difference in operating costs between membrane, diaphragm, and mercury plants results from variations in electricity and steam consumption for the three processes. Table 9 provides a comparison of the energy consumption involved in the three cell technologies.

Table 11. **Investment for Chlorine Membrane Electrolysis Plant**

Item	Estimated investment (in 1000 US$)
cells	27,200
brine purification	14,000
chlorine processing	16,000
waste gas treatment	2,300
caustic evaporation	6,900
utilities	4,500
rectifiers	10,000
engineering	10,000
total	*90,900*

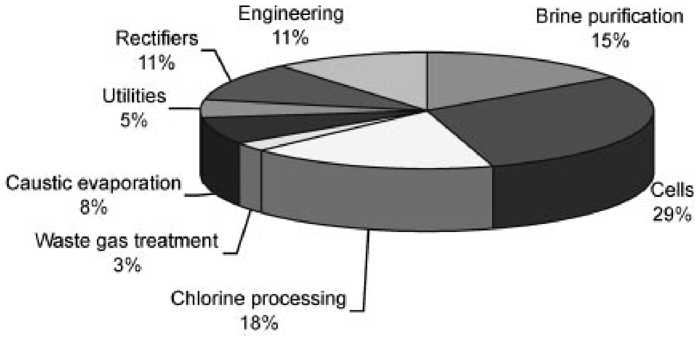


Fig. 30. Distribution of investment for a membrane chlor-alkali plant.

The cost of constructing a plant varies significantly with the actual plant configuration, procurement conditions, and the production capacity. A breakdown of the total investment for a grass root membrane electrolysis plant of ~160,000 mtpy of chlorine production capacity is given Table 11 and graphically in Figure 30.

Conversions from mercury to membrane technology require new facilities to protect the membranes from traces of mercury and place restrictions on the use of existing equipment. Diaphragm plants often are more easily adapted to the needs of membrane technology. Those plants that operate on a brine feed will require extensive revisions to achieve a water balance after conversion. See references (25, 107 and 108) for more details related to these capital costs.

7.1. Capacity. In the past, chlorine capacity was located close to its end use markets, which were primarily pulp and paper and vinyls products (ie, ethylene dichloride (EDC) [107-06-2] and vinyl chloride monomer (VCM) [75-01-4]). Other derivative demand was also located in close proximity to the chlorine source. Over time, world trade in chlorine through its derivatives has accelerated. Chlorine facilities have become larger to reduce the overall costs and capture economies of scale, and they are increasingly located in areas with low energy costs. The days of the small chlorine plants servicing a localized market are rapidly coming to an end, except possibly in the developing world.

The regions of North America, West Europe, and Northeast Asia have almost 75% of the world's chlor-alkali capacity (Fig. 31). Of these, only North

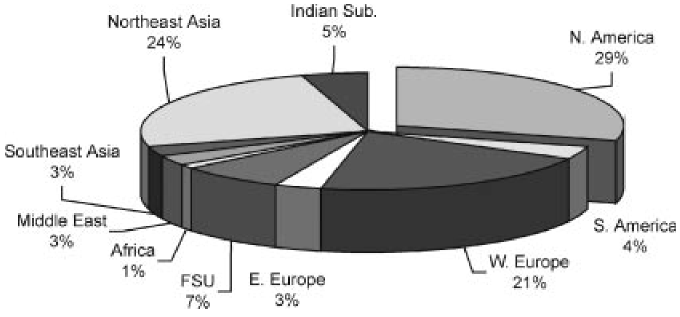


Fig. 31. Chlorine capacity in the world in 2000. Total capacity = 53×10^6 t (5,6).

America is and will remain a net exporter of chlorine equivalents. The Middle East possesses only 3% of the world's capacity, but it is a major net exporter of chlorine equivalents in the form of vinyl intermediates such as EDC. The driving force behind the location of new chlor-alkali facilities will be where electricity (energy) is available at a low cost. Large exports of vinyls and competitive electricity costs will reduce the overall costs and capture economies of scale. Although transportation of chlorine derivatives and caustic soda is a consideration, low cost power is the greatest concern.

Growth in chlorine derivatives is the key to understanding the addition of chlorine capacity around the world. Chlorine demand will increase with improving economic conditions, since chlorine is consumed in the manufacture of durable goods such as those used in infrastructure (PVC pipe, windows, and doors, polyurethane insulation). About 35% of total chlorine demand is consumed in vinyls (PVC) through the direct chlorination EDC process. The organic chemicals group, excluding vinyls, accounts for ~20% of the total chlorine demand and includes polycarbonates, toluene diisocyanate (TDI) and methylene (MDI) (for polyurethanes), epichlorohydrin, and propylene oxide. Both the vinyls and organics categories are forecast to require increasing volumes of chlorine, as the global economy improves.

7.2. U.S. Chlorine Market and Growth. The chlor-alkali industry went through a period of capacity rationalization during the mid-1980s. Then, the demand for chlorine derivatives changed from a regional or local market to a more global market. On a world basis, ~4 million metric tons of capacity were shut down during this period. The smaller, higher cost, and less environmentally friendly plants were the ones that were closed. The closure of these smaller plants set the stage for the larger, lower cost plants that have come on line during the 1990s.

Environmental issues concerning chlor-alkali facilities and some of the chlorine derivatives were very prevalent during the 1990s. Mercury cell chlorine plants faced strict limits on mercury emissions and they have, thus far, succeeded in meeting all of the standards placed on them. Mercury cells have been phased out in Japan for environmental reasons and there is an agreed time table for their phase-out in Europe. Several of the chlorine derivatives have encountered their own environmental roadblocks, such as

- Dioxin issues with pulp and paper.
- Banning of some fluorocarbons.
- Carbon tetrachloride being almost eliminated.
- Restricted emissions of chlorinated solvents.
- PVC in bottling and packaging (non durable) markets.

Environmental issues will continue to shape the industry. However, the benefits of chlorine and its derivatives will significantly outweigh its alleged hazards. The chlorine industry will continue to actively promote the use of chlorine, based on its contribution to society and its favorable environmental impact, which is based on "cradle to grave" scientific analysis.

Technology has also played a significant role in the shaping of the chlor-alkali industry. Most of the early plants used mercury cell technology and

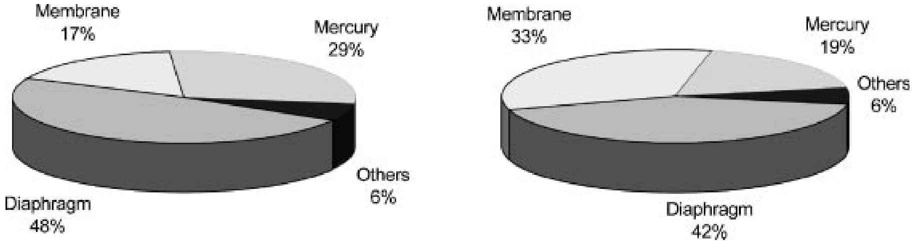


Fig. 32. Chlor-alkali technologies in 1990 and 2000. 1990 Capacity $= 45.0 \times 10^6$ t; 2000 Capacity $= 53.0 \times 10^6$ t. (5,6).

then diaphragm plants took a larger percentage of total world capacity. Today, membrane technology is the technology of choice. This progression was driven by local economic factors and the advancement of technology (Fig. 32). The trend to membrane cells is due to their lower operating costs and to environmental concerns over mercury and asbestos. Figures 33 and 34 show the locations of U.S. chlorine plants in 2000. Table 12 depicts U.S. capacity information for the period 1990–2000.

The data represent elemental chlorine only and do not include chlorine in the form of HCl. More than 95% of total HCl produced in the United States is the result of a chlorine-using process. In general, processes that use chlorine consume about one-half of the chlorine in the process and convert the other one-half to HCl. Hydrogen chloride can be marketed in either the aqueous or the anhydrous form.

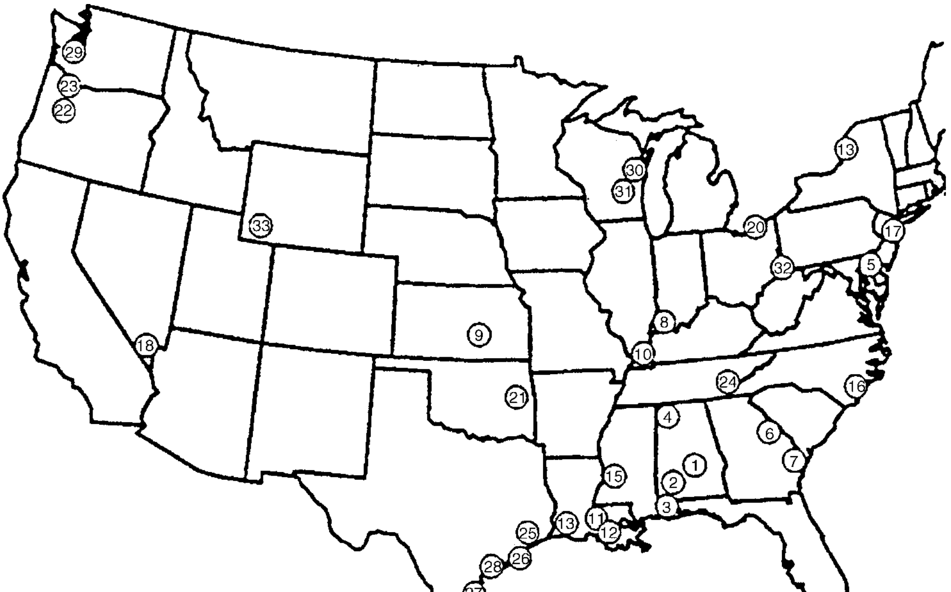


Fig. 33. Chlorine producing locations in the United States (5,6). See Fig. 34 for key.

United States
Chlor-alkali producing locations

1 Burkville, Alabama
  GE Plastics (CHL/CAU)
2 Mcintosh, Alabama
  Olin (CHL/CAU)
  Sunbelt(CHL/CAU)
3 Mobile, Alabama
  Oxy (CHL)
4 Muscle Shosis, Alabama
  Oxy (CHL)
5 Delaware City, Delaware
  Oxy (CHL/CAU)
6 Augusta, Georgia
  Olin (CHL/CAU)
7 Rincon, Georgia
  Ft. Howard (CHL/CAU)
8 Mount Vermon, Indiana
  GE Plastics (CHL/CAU)
9 Wichita, Kansas
  Vulcan (CHL/CAU)
10 Calvert City, Kantucky
  Westlake (CHL/CAU)
11 Baton Rouge/ Plaquemine/
  St.Gabriel, Louisiana
  FPC USA (CHL/CAU)
  Dow (CHL/CAU)
  George Gulf (CHL/CAU)
  Pioneer Chlor (CHL/CAU)
12 Convent/Geismar/
  Gramercy/Taft, Louisiana
  Oxy (CHL/CAU)
  Vulcan (CHL/CAU)
  Vulcan C-A (CHL/CAU)
  LaRoche (CHL/CAV)
13 Lake Charles, Louisiana
  PPG (CHL/CAU)
14 Orrington, Maine
  Hotrachem Mfg (CHL/CAU)
15 Vicksburg, Mississippi
  Cedar (CHL)
16 Acme, North Carolina
  Hottrachem Mfg (CHL/CAU)
17 South Kearny, New Jersey
  Kuchne (CHL/CAU)
18 Handerson, Nevada
  Pioneer Chlor (CHL/CAU)
  TIMET (CHL)
19 Niagara Falls, New York
  Du Pont (CHL)
  Olin (CHL/CAU)
  Oxy (CHL/CAU)
20 Ashtabula, Ohio
  Ashta (CHL)
21 Muskogee, Oklahoma
  Ft. Howard (CHL/CAU)
22 Albany, Oregon
  Oregon Metail (CHL)
23 Portland, Oregon
  Atolina (CHL/CAU)
24 Charteston, Tennessea
  Olin (CHL/CAU)
25 Baytown/Deer Park/
  LaPorte, Texas
  Bayer (CHL/CAU)
  Oxy Vinyls (CHL/CAU)
26 Freeport, Texas
  Dow (CHL/CAU)
27 Ingleside, Texas
  Oxy (CHL/CAU)
28 Point Comfort, Texas
  FPC USA (CHL/CAU)
29 Tacoma, Washington
  Pioneer Chlor (CHL/CAU)
30 Green Bay, Wisconsin
  Ft. Howard (CHL/CAU)
31 Port Edwards, Wisconsin
  Vulcan (CHL) (CAU)
32 Natrium, West Virginia
  PPG (CHL/CAU)
33 Granger/Green River, Wyoming
  FMC Wyoming (CAU)

Fig. 34. Key to the numbers in Figure 33.

Aqueous HCl (muriatic acid) is a solution of about two-thirds H_2O and one-third HCl. Anhydrous HCl is used primarily as a source of chlorine for the production of EDC, the precursor of VCM. The VCM production itself accounts for 65% of total production of HCl in the United States, but it is not a source of muriatic acid because all the HCl is recycled through the oxychlorination process to EDC.

Most anhydrous HCl goes into the captive or nonmerchant market. The distinguishing difference between the two forms of HCl is that the anhydrous material moves almost exclusively by pipeline while muriatic acid moves by trucks, tank cars, and barges. Clearly, transporting muriatic acid is expensive because more than one-half of the volume is water. Therefore, the muriatic acid market tends to be regional and there is almost no international trade. The U.S. muriatic acid market is split among the Northwest, Northeast, and Gulf Coast regions. The Northwest and Northeast markets are smaller than that of the Gulf Coast and are supplied largely by acid manufactured by chlor-alkali producers, by direct reaction of hydrogen with chlorine.

The Gulf Coast market is by far the dominant regional market in volume, but it is characterized by significantly more by-product HCl. Large HCl producers on the Gulf Coast include isocyanate and fluorocarbon producers. These industries are significant sources of HCl, and its supply therefore is a function of the demands for their products. Recognizing this is the key to understanding

Table 12. **Chlorine Capacities**^{a}

			Average Annual Capacities, (-000- Metric Tons)											
Company United States	Location	Process	1995	1996	1997	1998	1999	*2000*	2001	2002	2003	2004	2005	Remarks
Ashta	Ashtabula, Ohio	(8)	40	40	40	40	40	*40*	40	40	40	40	40	from LinChem/ KOH
ATOFINA	Portland, Oreg.	(1)						*85*	45	(170)	(170)	(170)	(170)	
		(2)						*17*	8	(34)	(34)	(34)	(34)	
Bayer	Baytown, Tex.	(2)					284	*310*	310	310	310	310	310	Ku Tech
		(4)	62	82	82	82	(82)	*40*	80	80	80	80	80	KU Tech
BF Goodrich	Calvert City, Ky.	(3)	111	111	83									To Westlake
Cedar	Vicksburg, Miss.	(9)	36	45	45	45	45	*45*	45	10	(45)	(45)	(45)	from Vertac Chemcial Co.
Dow	Freeport, Tex.	(1)	2204	2264	2431	2431	2431	*2431*	2431	2431	2431	2431	2431	
		(2)					75	*450*	500	500	500	500	500	Asahi Chem. magnesium
		(5)	250	250	250	75	(250)	*(250)*						
	Plaquemine, La.	(1)	525	525	525	525	525	*525*	525	525	525	525	(525)	
		(1)	745	745	745	745	745	*745*	745	745	745	745	745	
		(2)											655	Asahi Chem + 100 Planne
Du Pont	Corpus Christi, Tex.	(4)												
	Niagara Falls, N.Y.	(5)	77	77	77	77	77	*77*	77	77	77	77	77	no caustic

Table 12 (*Continued*)

Company United States	Location	Process	Average Annual Capacities, (-000- Metric Tons)											Remarks
			1995	1996	1997	1998	1999	*2000*	2001	2002	2003	2004	2005	
Elf Atochem	Portland, Oreg.	(1)	170	170	170	170	170	*85*						built 1947
		(2)	34	34	34	34	34	*17*						built 1990
Fort James	Green Bay, W.S.	(1)			8	(8)								
	Muskogee, Okla.	(2)			5	(5)								
	Rincon, Ga.	(2)			6	(6)								
FPC USA	Baton Rouge, La.	(1)	216	216	216	236	236	*236*	236	236	236	236	236	
	Point Comfort, Tex.	(2)	654	654	654	690	798	*798*	798	798	798	798	798	Expn Planned; Chl. Engr. T
Ft. Howard	Green Bay, Wis.	(1)	8	8										built 1968; to Fort James
	Muskogee, Okla.	(2)	5	5										to Fort James
Ft. Howard	Rincon, Ga.	(2)	6	6										built 1990; to Fort James
GE Plastics	Burkville, Ala.	(1)	24	24	24	24	24	*24*	24	24	24	24	24	built 1987
	Mount Vernon, Ind.	(1)	50	50	50	50	50	*50*	50	50	50	50	50	built 1976
Georgia Gulf	Plaquemine, La.	(1)	427	427	427	427	427	*427*	427	427	427	427	427	from Georgia Pacific
Georgia Pacific	Bellingham, Wash.	(3)	82	82	82	82	48	*(82)*						built 1965 from Brunst P&P
	Brunswick, Ga.	(3)												
Holtrachem Mfg	Acme, N.C.	(2)					8	*40*	(50)					OxyTech; permanent shutdown

		(3)	48	48	48	48	12	*(48)*						
	Orrington, ME	(3)	73	73	73	73	73	*50*	(73)					permanent shutdown
Hooker Chemical	Tacoma, Wash.	(1)												to Oxy
	Taft, La.	(1)												to Oxy
Hooker/IMC JV	Niagara Falls, N.Y.	(1)												some KOH;
Kuehne	S.Kearny, N.J.	(2)					8	*16*	16	16	16	16	16	ICI Tech.
La Roche	Gramercy, La.	(1)	180	180	180	180	180	*180*	90	(180)	(180)	(180)	(180)	from Kaiser
Magnesium	Rowley, Utah.	(5)	18	18	18	18	18	*18*	18	18	18	18	18	from Renco
Miles	Baytown, Tex.	(4)	20											to Bayer
Niachlor	Niagara Falls, N.Y.	(2)	218											
Olin	Augusta, Ga.	(3)	102	102	102	109	109	*109*	109	109	109	109	109	built 1965
	Charleston, Tenn.	(3)	236	236	236	245	245	*245*	245	245	245	245	245	built 1962
	McIntosh, Ala.	(1)	364	364	364	364	364	*364*	364	364	364	364	364	
	Niagara Falls, N.Y.	(2)		218	218	218	218	*218*	218	218	218	218	218	
Oregon Metallurgical	Albany, Oreg.	(5)	5	5	5	5	5	*5*	5	5	5	5	5	built 1971
Oxychem	Convent, La.	(1)	336	336	336	336	336	*336*	336	336	336	336	336	built 1981; From diamond Sh.
Oxychem	Deer Park, Tex.	(1)	248	248	248	248	83							
		(3)	100	100	100	100	33							built 1958
	Delaware City, Del.	(3)	74	74	74	74	74	*74*	74	74	74	74	74	built 1965; from diamond Sh.

Table 12 (*Continued*)

Company United States	Location	Process	1995	1996	1997	1998	1999	*2000*	2001	2002	2003	2004	2005	Remarks
		Average Annual Capacities, (-000- Metric Tons)												
		(8)	61	61	61	61	61	*61*	61	61	61	61	61	from KCl; From diamond Sh.
	Ingleside, Tex.	(1)	455	455	455	513	571	*571*	571	571	571	571	571	built 1974; From Du Pont
	La Porte, Tex.	(1)	479	500	500	500	167							built 1974; From diamond Sh.
	Mobile, Ala.	(7)	41	41	41	41	41	*41*	41	41	41	41	41	
	Muscle Shoals, Ala.	(8)	132	132	132	132	132	*132*	132	132	132	132	132	only KOH after 92; From Di Sham.
	Niagara Falls, N.Y.	(1)	293	305	305	305	305	*305*	305	305	305	305	305	built 1898; From Hooker/IMC
	Tacoma, Wash.	(1)	105	105	52									From Hooker To Pioneer
		(2)	101	101	50									to Pioneer
	Taft, La.	(1)	473	473	473	473	473	*473*	473	473	473	473	473	built 1966; From Hooker
		(2)	115	115	146	177	177	*177*	177	177	177	177	177	
Oxy Vinyls LP	Deer Park, Tex.	(1)					165	*248*	248	(248)	(248)	(248)	(248)	41 on hold
		(3)					67	*100*	100	(100)	(100)	(100)	(100)	
	La Porte, Tex.	(1)					333	*500*	500	500	500	500	500	

Pioneer	Henderson, Nev.	(1)	138	138	138	138	138	*138*	138	138	138	138	138	built 1942; From Stauffer
	St. Gabriel, La.	(3)	179	179	179	179	179	*179*	179	179	179	179	179	built 1970; From Stauffer
	Tacoma, Wash.	(1)			53	105	105	*105*	105	17	(105)	(105)	(105)	from Oxy
		(2)			51	101	101	*101*	101	16	(101)	(101)	(101)	from Oxy
PPG	Lake Charles, La.	(1)	1000	1000	1000	1000	1000	*1000*	1000	1000	1000	1000	1000	
PPG	Lake Charles, LA	(3)	180	180	180	180	180	*180*	180	180	180	180	180	
	Natrium, WV	(1)	270	270	270	270	270	*270*	270	270	270	270	270	
		(3)	91	91	91	91	91	*91*	91	91	91	91	91	built 1943
Sunbelt	McIntosh, AL	(2)			52	227	227	*227*	227	227	227	227	227	KU Tech.
TIMET	Henderson, NV	(5)	5	5	5	5	5	*5*	5	5	5	5	5	
Vulcan	Geismar, LA	(1)	248	248	248	248	248	*248*	248	248	248	248	248	
	Port Edwards, WI	(3)	45	45	45	45	45	*37*	35	35	35	35	35	built 1967
		(8)	42	42	42	42	42	*50*	53	53	53	53	53	from KCL + Mercury Cel
	Wichita, KS	(1)	165	165	165	165	165	*165*	165	165	165	165	165	built 1952
		(2)	83	83	83	83	83	*83*	83	83	83	83	83	1st U.S. membrane tech
Vulcan C-A	Geismar, LA	(2)						*98*	195	195	195	195	195	Mitsui jv
Westlake	Calvert City, KY	(2)								155	155	155	155	Asahi Chem Tech
		(3)			28	111	111	*111*	111	(111)				From BFG; DeNora Tech

Table 12 (*Continued*)

Average Annual Capacities, (-000- Metric Tons)														
Company United States	Location	Process	1995	1996	1997	1998	1999	*2000*	2001	2002	2003	2004	2005	Remarks
	Lake Charles, LA	(2)												+360 delayed indefinitely
Weyerhaeuser	Longview, WA	(1)	160	160	160	160	27	*(160)*						built 1957
Subtotal	(1) Diaphragm cell		9283	9376	9543	9613	9538	*9511*	9296	8825	8808	8808	8283	
Subtotal	(2) Membrane cell		1216	1216	1299	1530	2013	*2552*	2633	2695	2679	2679	3334	
Subtotal	(3) Mercury cell		1321	1321	1321	1337	1267	*1176*	1124	913	913	913	913	
Subtotal	(4) From HCl		82	82	82	82		*40*	80	80	80	80	80	
Subtotal	(5) With metal production		355	355	355	180	105	*105*	105	105	105	105	105	
Subtotal	(7) From KCl+ Membrane Cell		41	41	41	41	41	*41*	41	41	41	41	41	
Subtotal	(8) From KCl+ Mercury Cell		275	275	275	275	275	*283*	286	286	286	286	286	
Subtotal	(9) Other		36	45	45	45	45	*45*	45	10				
TOTAL	United States		12609	12711	12961	13103	13284	13753	13610	12955	12912	12912	13042	

[a] *Note*: Capacities shown in parentheses refer to units that are not operating; however, the equipment is still present, i.e. mothballed.

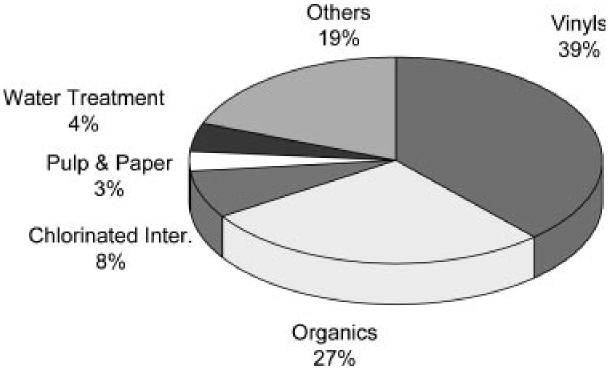


Fig. 35. Chlorine demand in the United States in 2000. Domestic demand = 13.2×10^6 t. (5,6).

the merchant market. Isocyanate producers have worked to couple capacity and HCl production with HCl disposal strategies. Fluorocarbon producers have not, as yet, developed a similar strategy to couple HCl production with its disposal.

Besides its consumption in the vinyls industry, HCl is used in a variety of industrial applications, ranging from chemical manufacturing to steel production, oil and gas well acidization, and food processing.

Low cost energy and raw materials and well-developed infrastructure make the United States one of the most attractive locations for chlor-alkali and derivative capacity. The vinyls market represents almost 40% of the domestic chlorine demand, followed closely by the Others and Organics sectors at 19 and 27%, respectively (Fig. 35).

Most of the major U.S. vinyls producers are integrated into chlorine or have access to chlorine through a joint venture partner. Shintech is the notable exception, with chlorine supplied in the form of VCM from Dow. During the past 10 years or so, there has been consolidation in the U.S. vinyls industry, and the number of PVC producers declined as a result. Many of the remaining producers have strengthened their positions by integrating downstream into compounded and fabricated products. Despite a slowdown in demand growth in 1998–1999 and in late 2000–2001, the United States is, and will continue to be, a primary supplier of vinyls to the international market. Growth in export and domestic vinyls demand will increase the chlorine consumption into this end use by an average of ~4–5% per year through 2005.

In the Organics sector, PO, epichlorohydrin (epi), TDI, MDI, and polycarbonates all will exhibit growth at or above GDP. The total growth for this end use group is forecast to be 3.8%/year, with PO as the dominant component. Polycarbonates is one of the smaller components but will experience the largest growth rate. Titanium dioxide is one of the components of the Inorganics market segment, which is included on the graph in the Others category. Chlorine and caustic soda are used in the manufacturing of wood pulp. Because of environmental pressure, the industry is now moving towards elemental chlorine-free pulp bleaching, and demand for chlorine from pulp bleaching was expected to be

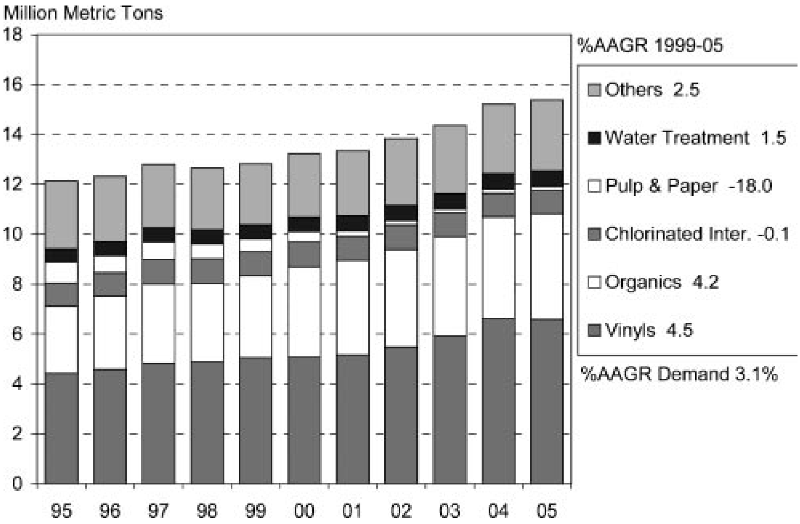


Fig. 36. Chlorine demand in the United States (5,6).

greatly reduced by the end of 2001. Caustic soda, however, will continue to be required in the pulp process.

With U.S. chlorine demand projected to increase faster than chlor-alkali capacity, operating rates will be at a maximum by 2003–2004 (Fig. 36). Additional capacity is expected to be installed to satisfy the anticipated chlorine demand.

The end use pattern for caustic soda (Fig. 37) in the United States closely resembles that for the entire world, where pulp accounts for ~21% of the total

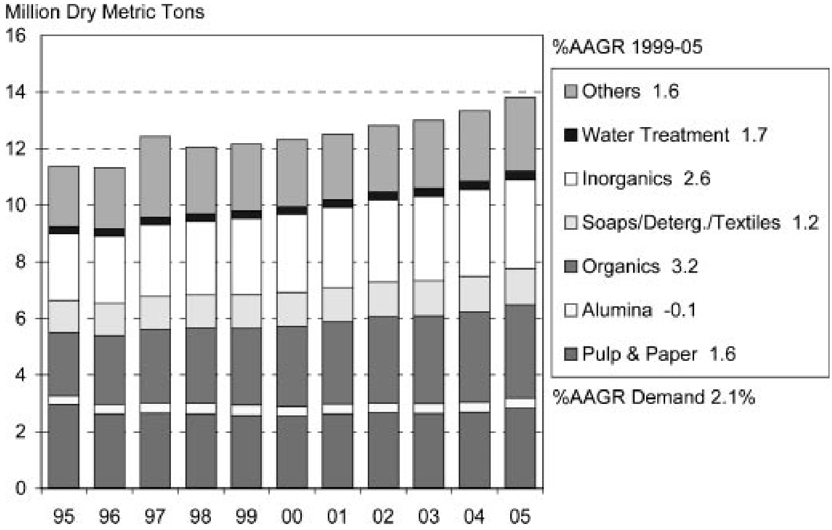


Fig. 37. Caustic demand in the United States (5,6).

United States domestic demand and is forecast to consume a modest 1.6% per year more caustic soda until 2005. Although 68% of the region's pulp capacity is located in the United States, most of the pulp is integrated into paper, in contrast to Canada, where about one-half of the pulp production is sold as market pulp. This means that consumption of caustic soda is impacted by the net trade position of the U.S. paper and paperboard industries. When paper and paperboard imports rise causing domestic paper and paperboard operating rates to decline, pulp producers cannot move the pulp into the market pulp market and pulp operating rates will decline as well.

The alumina sector is a relatively small player in the United States. However, this sector is the destination of more than one-half of the U.S. caustic soda exports. When end use markets of the U.S. caustic soda exports are considered in a total demand analysis, the alumina sector accounts for ~10% of the total U.S. caustic soda production.

The "Others" category includes many miscellaneous consumers, including petroleum refining and caustic soda consumption that can be switched to and from soda ash. There is an estimated 400,000 dry metric tons of caustic soda that could be switched to soda ash for applications such as pulp, sodium silicates, sodium chromates, and soaps/detergents. Caustic soda consumption into these switchable applications has not been anywhere close to the 400,000 dry metric ton level since the early 1990s. Based on Chemical Market Associates, Inc (CMAI) projections of caustic soda and soda ash prices for the next few years, soda ash producers have a larger than usual window of opportunity to secure additional volume from caustic soda. It is surmised that a minimal amount of caustic soda will still be consumed into some switchable applications due to specific circumstances.

Exports from the United States constitute ~12% of the total caustic soda market and will continue to be a key source in supplying caustic soda to the international market. The expected growth in exports of >9%/year will support overall demand growth of 3%/year for caustic soda. The relative net export volume for the United States is illustrated in Figure 38, as the difference between the production and demand bars.

With the start up of new 215,000 dry metric tons per year Vulcan/Mitsui caustic plant during 2000, there is very little additional nameplate capacity scheduled for the future. Formosa has announced a 235,000 dry metric ton membrane unit for Baton Rouge, Louisiana, which is targeted for a 2004 start up. Westlake intends to build a 171,000 dry metric ton membrane unit at Calvert City, Kentucky, replacing its existing 122,000 dry metric ton mercury cell unit.

The domestic requirements for chlorine, to support rising vinyls exports, will require additional chlor-alkali capacity. Higher operating rates and improving margins over the next couple of years will help to justify this additional capacity.

7.3. Chlorine/Caustic Balance. The operating rate of a chlor-alkali unit is determined by the demand for chlorine, which means that the caustic supply is determined by chlorine demand and not caustic demand. In a typical cycle, chlorine demand (and market price) will increase first with improving economic conditions, since chlorine end uses are consumed in long term durable goods such as the construction of infrastructure (PVC pipe, windows, and

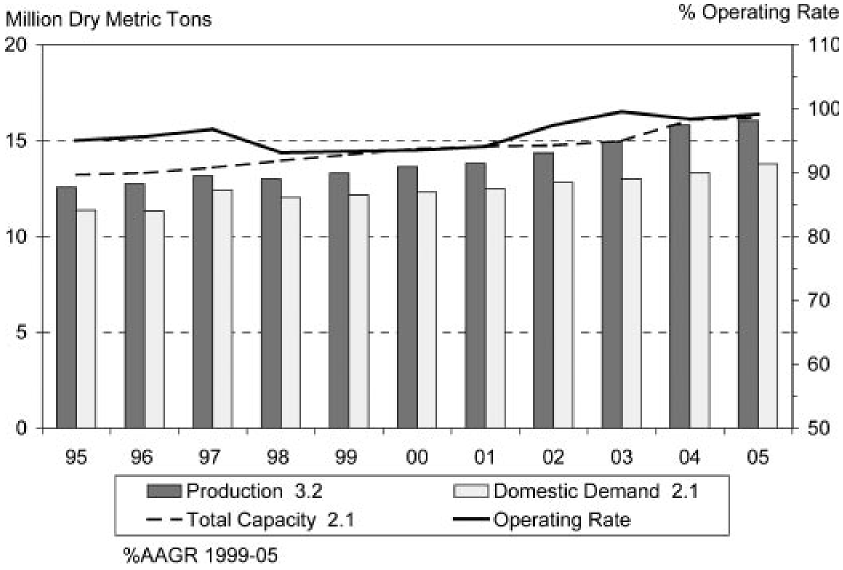


Fig. 38. Chlorine and caustic demand in the United States (5,6).

doors, polyurethane insulation); ~55% of total chlorine demand is consumed in PVC and polyurethane applications. Caustic soda end uses are more diverse and cause caustic soda demand to react more slowly to improving economic conditions. The resultant impact on caustic soda prices is downward pressure. As chlorine demand rises, prices will rise and more chlor-alkali (chlorine and caustic soda) will be produced. The slower acting caustic soda demand will not be able to consume the additional caustic supply in a timely manner and caustic soda prices will weaken. As caustic soda demand catches up with its supply, the tightening supply/demand balance will provide market support for higher caustic soda prices. The objective of the chlor-alkali producers is to maximize the price of an ECU (electrochemical unit), not just chlorine or just caustic soda prices.

The U.S. production ratio of caustic to chlorine is below the theoretical ratio of 1.1 ton of caustic soda for each one ton of chlorine, because ~4% of the chlorine capacity does not coproduce caustic soda. Most of these units coproduce potassium hydroxide, while some produce a molten metal. The U.S. exports are an important end use for domestically produced caustic soda, and ~12% of the total production is exported.

8. Analytical Methods

Industrial liquid chlorine is routinely analyzed by established procedures (9,13) for moisture, chlorine, other gaseous components, bromine nitrogen trichloride, and mercury. Moisture and nonvolatile matter are determined by evaporation at ambient temperature, followed by gravimetric measurement of the residue (109). Free chlorine levels are estimated quantitatively by thiosulfate titration of the iodine liberated by addition of excess acidified potassium iodide to a gas mixture.

9. Health and Safety Factors

No one should attempt to handle chlorine for any purpose without a thorough understanding of its properties and the hazards involved. Standard safety books and handbooks contain much of this information (110–112). Industry organizations such as The Chlorine Institute and Euro Chlor have active programs to create and maintain a series of pamphlets and manuals that address various issues such as plant operation, piping design and layout, storage system design and practices, transportation, and emergency procedures. Among these, *The Chlorine Manual* (11), which has been approved as an American National Standard, can be recommended as a single source of basic information and listing of important references.

Chlorine is a respiratory irritant and is readily detectable at concentrations <1 ppm in air because of its penetrating odor. Chlorine gas, after several hours of exposure at ~ 1 ppm causes mild irritation of the eyes and mucous membranes of the respiratory tract. At high concentrations and in extreme situations, increased difficulty in breathing can result in death through suffocation. The physiological response to various concentrations of chlorine appears in Table 13.

Manufacture of chlorine presents the usual hazards found in the chemical industry and the specific hazard of live electrical equipment at modest to high voltage in the elecrrolysis area. Standard safety gear includes electrically resistant boots and gloves for those working in the electrolysis area and escape respirators for all personnel and visitors in the chlorine production area. Other specialized safety equipment is necessary for various operations, and this is discussed in the appropriate manuals.

A standard feature on chlorine plants is a scrubbing system containing an alkaline solution (usually NaOH). This removes chlorine from vent streams, whether continuously flowing or present only in emergency situations. The low pressure side of the chlorine process usually is protected by water seals or mechanical relief devices, depending on the operating pressure. Any vent

Table 13. **Physiological Response to Chlorine**

Parameter	Parts of chlorine per million parts of air (volume)
least amount required to produce slight symptoms after several hours of exposure	1
least detectable odor	3.5
maximum amount that can be inhaled for 1 h without serious physiological response	4
least amount required for throat irritation	15
least amount required to induce coughing	30
amount causing severe symptoms in 30–60 min	40–60
LD_{50}	
humans, in 30 min	840
rats, in 60 min	290
mice, in 60 min	137
amount expected to affect aquatic life	<0.1

gas from these devices flows to the scrubbing system before discharge to the atmosphere.

10. Uses

Figure 39 depicts the chlorine demand for various end-uses (see also Tables 3 and 4).

Phosgene is made by reacting carbon monoxide with chlorine in the presence of activated carbon. It is the starting material for the manufacture of polycarbonates, TDI, and MDI. Polycarbonate (PC) resins are engineering thermoplastics that are produced by reacting phosgene and bisphenol A (BPA). The PC resins are typically characterized by high impact strength, dimensional stability, transparency, and excellent electrical properties. In addition to general purpose polycarbonate resins, a variety of specialty materials, blends, and alloys are also available. Polycarbonates are widely used, with applications in the automotive industry, glazing, electronics, computers and business machines, and for software, audio and video compact discs (CDs, DVDs).

TDI is a major raw material for producing urethane foam, both flexible and rigid. Flexible urethane foams, by far the largest TDI end use, are used as bedding, furniture cushioning, carpet underlay, and packaging. MDI is used almost exclusively to make polyurethanes. MDI-based rigid urethane foams have the lowest thermal conductivity of any common insulation material. The largest insulation uses for these foams are in construction, refrigerators and freezers, and refrigerated rail cars and trucks. Rigid foams also have excellent buoyancy, and have been used in life-saving gear, swimming pools, sporting goods, and other flotation devices.

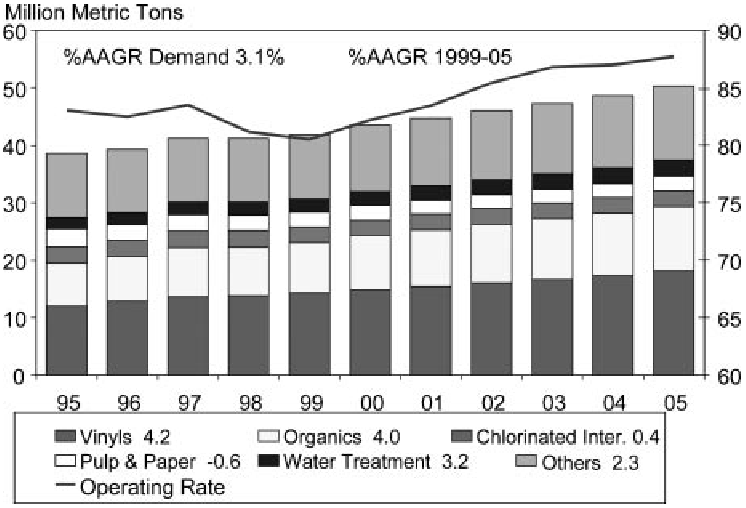


Fig. 39. World chlorine demand (5,6) (% AAGR refers to % average aggregate growth rate).

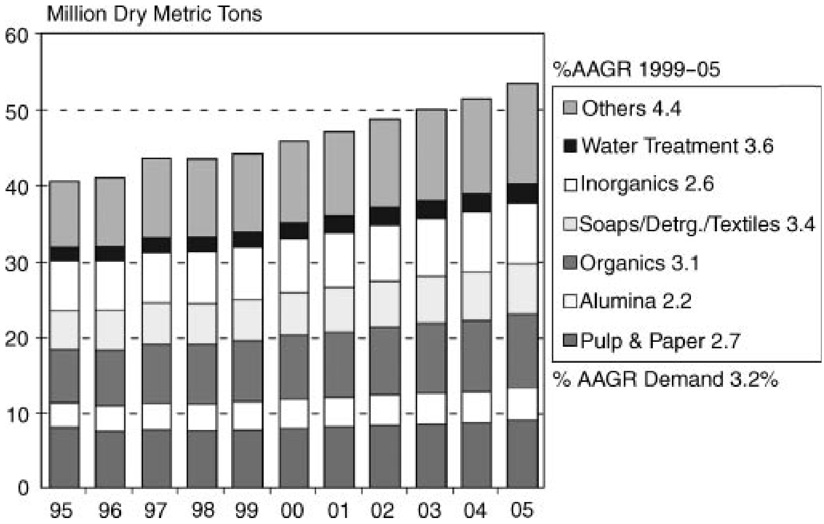


Fig. 40. World caustic demand (5,6) (% AAGR refers to % average aggregate growth rate).

Most epoxy resins are made from BPA and epi [106-89-8]. The chlorination of propylene produces allyl chloride which, when dehydrochlorinated with caustic soda, produces epi. Lime can also be used in this process, but disposal of the calcium chloride by-product creates strong opposition from environmentalist groups. Epoxy resins, used in making protective coatings, laminates, and fiber-reinforced composites, are the largest end use for epi. The second largest end use is synthetic glycerin, produced by the hydrolysis of epi with caustic soda. Production of synthetic glycerin has declined in recent years because of competition from natural material. Glycerin is used in the pharmaceutical, tobacco, cosmetics, and food and beverage industries.

Chlorine and propylene are used in the chlorohydrin process to produce propylene oxide (PO) [75-56-9]. In the chlorohydrin process, propylene reacts with chlorine to make propylene chlorohydrin, which is then dehydrochlorinated with caustic soda to make propylene oxide. An alternative process competing with this route is the direct oxidation of propylene. PO is a highly reactive alkyl epoxide used principally as a chemical intermediate. The largest application for PO is as a raw material for polyether polyols. Polyether polyols are used in polyurethane applications including flexible and rigid foams, elastomers, coatings, adhesives, and reaction injection molding polymers. PO can also be reacted with water to form propylene glycol, a raw material for unsaturated polyester resins. A few applications of unsaturated polyester resins include tubs and showers, gasoline tanks, and boat hulls. Dow is the largest producer of PO using the chlorohydrin process.

Actual declines in the use of chlorine in chlorinated intermediates (chloromethanes and chloroethanes) and pulp and paper are expected because of environmental concerns in these applications.

Chlor-alkali plants are built and operated to satisfy chlorine demand, not caustic demand. Chlorine demand is much more volatile than caustic demand

and reacts more quickly to changes in economic conditions. Over time, it is expected that both chlorine and caustic soda demand will increase by the same average annual rate and both trend with GDP.

Compared to chlorine, the market for caustic soda adapts more slowly to changing economic conditions, because of the diversity of its end uses (Fig. 40). Consumption of caustic soda in pulp mills is the largest single end use at 17%, which is about one-half of the size of the vinyl segment for chlorine consumption.

Alumina is the second largest end use for caustic soda at 8%, and demand for alumina is driven by aluminum metal. About one-third of aluminum is consumed by the transportation sector and ~15% by the construction sector, both of which are dependent on global economic health. The organics category is a fairly large segment and is a collection of many organic chemicals, including PO, epi, TDI and MDI (isocyanates), and polycarbonates.

11. Acknowledgments

The authors would like to thank Manfred Quissek of Q Group Inc. for providing us with the latest information on the transformers and rectifiers, Rick Romine of ELTECH systems for updating us on the developments in the diaphragm cell technologies, and K. Sambamurthy of Krupp-Uhde for encouragement during the course of the manuscript preparation and for providing clarifications on the current developments in the chlor-alkali technologies.

BIBLIOGRAPHY

"Alkali and Chlorine Industries" in *ECT* 1st ed., Vol. 1, pp. 358–430, by Z. G. Deutsch, Deutsch and Loonam; "Alkali and Chlorine Industries" in *ECT* 2nd ed., Vol. 1, pp. 668–758, by Z. G. Deutsch, Consulting Engineer, and C. C. Brumbaugh and F. H. Rockwell, Diamond Alkali Company; "Alkali and Chlorine Products, Chlorine and Sodium Hydroxide" in *ECT* 3rd ed., Vol. 1, pp. 799–865, by J. J. Leddy, I. C. Jones, Jr., B. S. Lowry, F. W. Spillers, R. E. Wing, and C. D. Binger, Dow Chemical U.S.A.; "Chlorine" in *ECT* 1st ed., Vol. 3, pp. 677–681, by D. G. Nicholson, University of Pittsburgh; "Chlorine" in *ECT* 2nd ed., Vol. 5, pp. 1–6, by D. G. Nicholson, East Tennessee State University; "Chlorine" in *ECT* 2nd ed., Supplement, pp. 167–177, by H. B. Hass, Chemical Consultant; "Alkali and Chlorine Products, Chlorine and Sodium Hydroxide" in *ECT* (online), posting date: December 4, 2000, by L. Calvert Curlin, OxyTech Systems, Inc., Tilak V. Bommaraju, and Constance B. Hansson, Occidental Chemical Corporation.

CITED PUBLICATIONS

1. *Chlor-alkali Consulting Service* (includes the monthly Chlor-alkali Market Report), Chemical Market Associates, Inc, Houston, Tex.
2. *World Chlor-alkali Analysis*, 1997, Chemical Market Associates, Inc, Houston, Tex.
3. *World Chlor-alkali Analysis*, 1998, Chemical Market Associates, Inc, Houston, Tex.
4. *World Chlor-alkali Analysis*, 1999, Chemical Market Associates, Inc, Houston, Tex.

5. *World Chlor-alkali Analysis*, 2000, Chemical Market Associates, Inc, Houston, Tex.
6. *World Chlor-alkali Analysis*, 2001, Chemical Market Associates, Inc, Houston, Tex.
7. S. Berthiaume, E. Anderson, and Y. Yoshida, *CEH Marketing Repoprt, Chlorine/Sodium Hydroxide, 733.1000A*, SRI International, Menlo Park, Calif., 2000.
8. R. Kapoor and J. J. Martin, *Thermodynamic Properties of Chlorine*, University of Michigan, Ann Arbor, Mich., 1957.
9. J. J. Martin and D. M. Longpre, *J. Chem. Eng. Data* **29**, 466 (1984).
10. *Properties of Chlorine in SI Units*, 2d ed., The Chlorine Institute, Washington, D.C., 1986.
11. Chlorine Institute, *The Chlorine Manual*, 6th ed., The Chlorine Institute, Washington, D.C., 1990.
12. CRA No, 188.04, *Assessment of the Economic Benefits of Chlor-Alkali Chemicals to the United States and Canadian Economies*, Charles River Associates, Boston, 1993.
13. *Chlorine Handbook*, Diamond Shamrock Chemical Co, Irving, Tex., 1984.
14. D. F. W. Hardie, *Electrolytic Manufacture of Chemicals from Salt*, The Chlorine Institute Inc, New York, 1975.
15. Brit. Pat. 1,147,442 (May 12, 1965), H. B. Beer (to Chemnor Corp.); 1,195,871 (Feb. 10, 1967), H. B. Beer (to ChemnorAG).
16. R. Kotz and S. Stucki, *Electrochim Acta* **31**, 1331 (1986).
17. T. Morimoto, T. Matsubara, and S. Ohashi, *Denki Kagaku* **60**, 649 (1992).
18. S. Trasatti, ed, *Electrodes of Conductive Metallic Oxides*, Parts A and B, Elsevier, Amsterdam, The Netherlands, 1980, 1981.
19. D. M. Novak, B. V. Tilak, and B. E. Conway, in J.O'M. Bockris, B. E. Conway, and R. E. White, eds, *Modern Aspects of Electrochemistry*, Vol. 14, Plenum Press, New York, 1982.
20. T. V. Bommaraju, C.-P. Chen and V. I. Birss, in J. Moorhouse, ed, *Modern Chlor-Alkali Technology*, Vol. 8, Blackwell Science, London, 2001 p. 57.
21. B. V. Tilak, V. I. Birss, J. Wang C.-P. Chen, and S. K. Rangarajan, *J. Electrochem. Soc.* **148**, **D109** (2001).
22. U.S. Pat. 5,948,222 (Sept. 7, 1999), C.-P. Chen and T. V. Bommaraju (to Occidental Chemical Corp.).
23. U.S. Pat. 6,156,185 (Dec. 5, 2000), C.-P. Chen and T. V. Bommaraju (to Occidental Chemical Corp).
24. J. E. Currey and G. G. Pumplin in J. J. MeKetta and W. A. Cunningham, eds., *Encyclopedia of Chemical Engineering and Design*, Vol. 7, Marcel Dekker, Inc, New York, 1978, p. 305.
25. P. Schmittinger, T. Florkiewicz, L. C. Curlin, B. Lüke, R. Scanell, T. Navin, E. Zelfel, and R. Bartsch in *Ullmann*'s *Encyclopedia of Industrial Chemistry*, 6th ed., Wiley-VCH Verlag GmbH, Weinheim, 1999, p. 1.
26. U.S. Pat. 4,410,411 (Oct. 18, 1983), R. W. Fenn, III, E. J. Pless, R. L. Harris, and K. J. O'Leary (to OxyTech Systems, Inc.).
27. U.S. Pat. 3,674, 676 (July 4, 1972), E. J. Fogelman (to OxyTech Systems, Inc.).
28. U.S. Pat. 3,928,166 (Dec. 23, 1975), K. J. O'Leary, C. P. Tomba, and R. W. Fenn, III (to OxyTech Systems, Inc.).
29. T. Florkiewicz, "Diaphragm Cell Improvements", Chlorine Institute meeting, New Orleans, La., March 14, 2001.
30. P. C. Foller, D. W. DuBois, and J. Hutchins, in S. Sealy, ed., "*Modern Chlor-Alkali Technology*", Vol. 7, p.162, Society of Chemical Industry, London, 1998.
31. F. Kuntzburger, D. Horbez, J. G. LeHelloco, and J. M. Perineau, in S. Sealy, ed., *Modern Chlor-Alkali Technology*, Vol. 7, p. 181, Society of Chemical Industry, London, (1998).

32. L. C. Curlin, T. V. Bommaraju, and C. B. Hansson, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Vol. 1, John Wiley & Sons, Inc., New York, 1991, p. 938.
33. *Diaphragm Cells*, OxyTech Systems, Inc, Chardon, Ohio, 1988.
34. U.S. Pat. 4,834,859 (May 30, 1989), L. C. Curlin and R. L. Romine (to OxyTech Systems, Inc.).
35. U.S. Pat. 3,591,483 (July 6, 1971), R. E. Loftfield and H. W. Laub (to OxyTech Systems, Inc.).
36. R. L. Romine and R. Matousek, *New and Improved Cell Hardware Designs*, a paper presented at the Electrode Corporation Chlorine/Chlorate Seminar, Sept. 15, 1998.
37. W. G. Grot, *Chem. Ing. Tech.* **44**, (1972) 167.
38. W. G. Grot, *Discovery and Development* of Nafion *Perfluorinated Membranes*, The Castner Medal Lecture, London International Chlorine Symposium, June, 1985.
39. J. L. Hurst, *Implementing Membrane Cell Technology within OxyChem Manufacturing*, International Symposium on Chlor-Alkali Industry, Tokyo, Japan, April, 1986.
40. *Perfluorinated Membranes* for *the Chlor-Alkali Industry*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1983.
41. D. L. Peet and J. H. Austin, *Nafion Perfluorinated Membranes, Operation in Chlor-Alkali Plants*, Chlorine Institute Plant Managers Seminar, The Chlorine Institute, Tampa, Fla., Feb. 1986.
42. *Nafion 90209, Product Bulletin*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1988.
43. *Nafion NX-961, Product Bulletin*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1984.
44. D. L. Peet, *Membrane Durability in Chlor-Alkali Plants*, Electrochemical Society Meeting, Honolulu, Hawaii, Oct. *1987; Proceedings of the Symposium on Electrochemical Engineering in the Chlor-Alkali and Chlorine Industries*, PV. No. 88-2, 1988, pp. 329–336.
45. U.S. Pat. 4,025,405 (1972), R. L. Dotson and K. J. O'Leary (to OxyTech Systems, Inc.).
46. H. Ukihashi, M. Yamabe, and H. Miyake, *Prog. Polym. Sci.* **12**, 229 (1986).
47. *Nafion Perfluorinated Membranes for KOH Production, Nafion Product Bulletin*, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1988.
48. *Nafion Perfluorinated Membranes, Introduction*, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1987.
49. Asahi Chemical Membrane Chlor-Alkali, Asahi Chemical Industry Co., Ltd., Tokyo, Japan, 1987.
50. T. D. Gierke and W. Y. Hsu, *Perfluorinated Ionomer Membranes*, A. Eisenberg and H. L. Yeager, eds. ACS Symposium Series, Washington, D.C., Vol. 180, 1982, p. 283.
51. D. Bergner, M. Hartmann, and R. Staab, *Chem.-Ing.-Tech.* **66**(6) 783 (1994).
52. N. M. Prout and J. S. Moorhouse, *Modern Chlor-Alkali Technology*, Vol. 4, Society of Chemical Industry, Elsevier Applied Science, London, 1990.
53. T. A. Davis, J. D. Genders, and D. Pletcher, *A First Course in Ion Permeable Membranes*, The Electrochemical Consultancy, Hants, U.K., 1997.
54. B. V. Tilak, A. C. R. Murthy, and B. E. Conway, *Proc. Indian Acad. Sci. (Chem. Sci.)* **97**, 359 (1986).
55. D. L. Caldwell, in J. O'M. Bockris, B. E. Conway, E. A. Yeager, and R. E. White, eds., *Comprehensive Treatise of Electrochemistry*, Vol. 2, Plenum Press, New York, 1981, Chapt. 2.
56. F. Hine, B. V. Tilak, and K. Viswanathan in R. E. White, J. O'M. Bockris, and B. E. Conway, eds., *Modern Aspects of Electrochemistry*, Vol. 18, Plenum Press, New York, 1986, Chapt. 5.

57. F. Hine, M. Yasuda, and M. Watanabe, *Denki Kagaku* **47**, 401 (1979).
58. U.S. Pat. 4, 024, 044 (May 17, 1977), J. R. Brannan and I. Malkin (to OxyTech Systems, Inc.).
59. Eur. Pat. Appl. 129, 734 (Jan. 2, 1985), N. R. Beaver, L. E. Alexander, and C. E. Byrd (to the Dow Chemical Co.); Eur. Pat. Appl. 129, 347 (Dec. 27, 1984), J. F. Cairns, D. A. Fenton, and P. A. Izard (to Imperial Chemical Industry PLC).
60. *CME Chlorine Engineers Membrane Electrolyzer*, Chlorine Engineers Corp. Ltd., Tokyo, Japan, 1989.
61. M. Esayian and J. H. Austin, *Membrane Technology for Existing Chlor-Alkali Plants*, presented at The Chlorine Institute, Feb. 1984.
62. *Japan's Chlor-Alkali Producers Save Energy by Retrofiting Diaphragm Cells* (Case History), E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.
63. *FM-21 SP Series Membrane Electrolyzer*, ICI Winnington, Northwich, Cheshire, England, 1989.
64. *MGC Monopolar Membrane Electrolyzer*, OxyTech Systems, Inc., Chardon, Ohio, 1988.
65. *Alkaline Chloride Electrolysis by the Membrane Process*, Krupp Uhde GmbH, Dortmund, Germany, 2001.
66. L. J. Gestaut, T. M. Clere, C. E. Graham, and W. R. Bennett, *Abstract No. 393*; L. J. Gestaut, T. M. Clere, A. J. Niksa, and C. E. Graha, *Abstract No. 124*, Electrochem. Soc. Meeting, Washington, D. C., Oct. 1983.
67. F. Gestermann and A. Ottaviani, *Modern Chlor-Alkali Technol.* **8**, 49 (2001).
68. K. Schneiders; A. Zimmermann; G. Henßen; *Membranelektrolyse—Innovation für die Chlor-Alkali-Industrie*; Forum Thyssen Krupp, 2/2001.
69. DE 19715429 A1, Bayer AG (Erfinder: Gestermann u.a., 15.10.1998, *"Elektrochemische Halbzelle"*.
70. EP–Pat. 0150017–1984, EP 0150018–1985; A. G. Hoechst, K.-H. Tetzlaff, D. Schmidt, and J. Russow.
71. K.-H. Tetzlaff and W. Wendel; *Elektrochemische Zellen als Fallfilmapparat*; *Chem.-Ing.- Tech.* 60 (1988) Nr. 7, S. 563.
72. Krupp Uhde GmbH, Dortmund; 2001.
73. M. T. Halbouty, *Salt Domes, Gulf Region, United States and Mexico*, p. 125, Gulf Publishing Co., Houston, Tex., 1967.
74. D. W. Kaufmann, Chapter 14, *Sodium Chloride*, ACS Monograph 145, Reinhold Publishing Co., New York, 1960.
75. E. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry—A Comprehensive Text*, 4th ed., John Wiley & Sons, Inc., New York, 1980, pp. 227 and 546.
76. J. A. Walkier, *Modern Chlor-Alkali Technology*, Ed. T. C. Wellington, Elsevier Appl. Science, London, Vol. 5, p. 233, 1992.
77. P. C. Westen, 'How to Use Steel and Titanium Safely,' *Proceedings, Third Euro Technical Chlor Seminar*, Paris, 1993. Reprinted in GEST 93/192.
78. J. S. Grauman and B. Willey, *Chem. Eng.* **105**(8), 106 (1998).
79. T. F. O'Brien and I. F. White, in R. C. Curry, ed., *Modern Chlor-Alkali Technology*, Royal Society of Chemistry, Cambridge, Vol. 6, p. 70, 1995.
80. T. F. O'Brien and I. F. White, S. Sealy, ed., *Modern Chlor-Alkali Technology*, Royal Society of Chemistry, Cambridge, Vol. 7, p. 202, 1998.
81. OxyTech Systems, Inc., *Chlorine Recovery Process*, Chardon, Ohio, (1988).
82. *Personal communication*, R. E. Shamel, Consulting Resources Corp. (2002).
83. K. Haas, *Electrochem. Techn.* **5**, 246 (1967).
84. K. Schneiders and C. Herwig, *Recycle of HCl to Chlorine*, 38th Chlorine Institute Plant Operations Seminar, Houston, Tex., 1995.
85. D. J. Eames and J. Newman, *J. Electrochem. Soc.* **142**, 3619 (1995).

86. C. W. Arnold and K. A. Kolbe, *Chem. Eng. Prog.* **48**, 167 (1971).
87. L. E. Bostwick and C. P. van Dijk, *Hydrogen Chloride to Chlorine: The Kel-Chlor Process*, 20th Chlorine Institute Plant Managers Seminar, New Orleans, La., 1977.
88. The M. W. Kellogg Co., *Hydrocarbon Process.* **60**(11), 143 (1981).
89. H. Y. Pan, R. G. Minet, S. W. Benson, and T. T. Tsotsis, *Ind. Eng. Chem. Res. 1994,* **33**, 2996.
90. U.S. Pat. 4,994,256, Feb. 1991, R. G. Minet, S. W. Benson, and T. T. Tsotsis.
91. M. Doyle and P. Arora, *J. Electrochem. Soc.* **148**, k1-k41 (2001).
92. *Chemical Marketing Reporter*, Sept. 4, 37 (2000); Sept. 11, 41 (2000).
93. http://www.eia.doe.gov/emeu/cabs/usa.html (2001).
94. C.-P. Chen, B. V. Tilak, and J. W. Quigley, *J. Appl. Electrochem.* **25**, 95 (1995).
95. C.-P. Chen and B. V. Tilak, *J. Appl. Electrochem.* **29**, 1300 (1997).
96. I. Rousar, V. Cezner, M. Vender, M. Kroutil, and J. Vachuda, *Chem. Prum.* **17/42**, 466 (1967).
97. W. Y. Hsu, J. R. Barkley, and P. Meakin, *Macromolecules* **13**, 198 (1980).
98. P. C. Rieke and N. Vanderborgh, *J. Membrane Sci.* **32**, 313 (1987).
99. H. Ukihashi, M. Yamabe, and H. Miyake, *Prog. Polym. Sci.* **12**, 229 (1986).
100. M. Quissek, *Personal Communication*, (2001).
101. GEST 79/81, Euro Chlor.
102. Pamphlets 6 and 60, The Chlorine Institute.
103. R. C. Talbot, *FRP Usage in the Chlorine Industry*, Bulletin No. 1704, Ashland Chemical Co., Columbus, Ohio.
104. K. Hannesen “*Materials of Construction for Handling Chlorine*,” Chlorine Safety Seminar, Brussels, 1990.
105. Pamphlet 95, Appendix A, The Chlorine Institute, Washington, D.C., 1997
106. GEST 73/20, Euro Chlor.
107. Y. C. Chen, *Process Economics Program Report*, Stanford Research Institute, Menlo Park, Calif., No. 61, 1970; No. 61A, 1974; No. 61B, 1978; No. 61C, 1982.
108. Abam Engineers, *Final Report on Process Engineering and Economic Evaluations of Diaphragm and Membrane Chloride Cell Technologies*, ANL/OEPM-80-9, Argonne National Laboratories, Argonne, Ill., Dec. 1980.
109. *ASTM Standard Test Method*: E410-86.
110. F. Lees, *Loss Prevention in the Process Industries*, 2 vols., Butterworths, London, 1980.
111. Compressed Gas Association, Inc., *Handbook of Compressed Gases*, 3rd ed., Van Nostrand Reinhold, New York, 1990.
112. R. J. Lewis, Sr., *Sax’s Dangerous Properties of Industrial Materials*, 8th ed., Van Nostrand Reinhold, New York, 1992.

GENERAL REFERENCES

D. W. Kaufmann, *Sodium Chloride*, ACS Monograph 145, Reinhold Publishing Co., New York, 1960.

J. S. Sconce, *Chlorine, Its Manufacture, Properties, and Uses*, Reinhold Publishing Corp., New York, 1962.

M. O. Coulter, ed., *Modern Chlor-Alkali Technology*, Ellis Horwood, London, 1980.

C. Jackson, ed., *Modern Chlor-Alkali Technology*, Vol. 2, Ellis Horwood, Chichester, 1983.

K. Wall, ed., *Modern Chlor-Alkali Technology*, Vol. 3, Ellis Horwood, Chichester, 1986.

N. M. Prout and J. S. Moorhouse, eds., *Modern Chlor-Alkali Technology*, Vol. 4, Elsevier Applied Science, London, 1990.

T. C. Wellington, ed., *Modern Chlor-Alkali Technology*, Vol. 5, Elsevier Applied Science, London, 1992.

R. W. Curry, ed., *Modern Chlor-Alkali Technology*, Vol. 6, Royal Society of Chemistry, Cambridge, 1995.

S. Sealey, ed., *Modern Chlor-Alkali Technology*, Vol. 7, Royal Society of Chemistry, Cambridge, 1998.

J. Moorhouse, ed., *Modern Chlor-Alkali Technology*, Vol. 8, Blackwell Science, Oxford, 2001.

W. Grot, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 16, Wiley-Interscience, New York, 1989.

P. Schmittinger, ed., *Chlorine—Principles and Industrial Practice*, Wiley-VCH, Weinheim, 2000.

F. Hine, *Electrochemical Processes and Electrochemical Engineering*, Plenum Press, New York, 1985.

Diaphragm Cells for Chlorine Production, Society of Chemical Industry, London, 1977.

F. Hine, R. E. White, W. B. Darlington, and R. D. Varjian, eds., *Proceedings of the Symposium on Electrochemical Engineering in the Chlor-Alkali and Chlorate Industries*, Proc. Vol. 88-2, The Electrochemical Society Inc., Pennington, N.J., 1988.

F. Hine, B. V. Tilak, J. M. Fenton, and J. D. Lisius, eds., *Proceedings of the Symposium On Performance of Electrodes for Industrial Electrochemical Processes*, Proc. Vol. 89-15, The Electrochemical Society Inc., Pennington, N.J., 1989.

Chlor-Alkali and Chlorate Technology: R. B. Macmullin Memorial Symposium, eds., H. S. Burney, N. Furuya, F. Hine and K.-I. Ota, Proc. Vol. 99-21, The Electrochemical Society Inc., Pennington, N.J., 1999.

Tilak V. Bommaraju
Process Technology Optimization, Inc

Benno Lüke
Glen Dammann, Krupp Uhde GmbH

Thomas F. O'Brien
Media, PA

Mary C. Blackburn
Chemical Market Associates, Inc.