

## Chapter 10

# Chlor-alkali Industries: Soda Ash, Caustic Soda, Chlorine

The manufacture of soda ash, caustic soda, and chlorine is one of the most important heavy chemical industries.<sup>1</sup> These chemicals rank close to sulfuric acid and ammonia in magnitude of dollar value of use. The applications are so diverse that hardly a consumer product is sold that is not dependent at some stage in its manufacture on chlorine and alkalies. The three products are sold almost entirely to industry for the production of soap and detergents, fibers and plastics, glass, petrochemicals, pulp and paper, fertilizers, explosives, solvents, and other chemicals.

**HISTORICAL.** The present synthetic process for the manufacture of soda ash is the Solvay process. Before this method was developed, the LeBlanc (1773) process was in universal use. It was based on roasting salt cake with carbon and limestone in a rotary furnace and subsequent leaching of the product with water. The crude product of the reaction was called *black-ash*. It was leached cold; whereupon some hydrolysis of sulfides took place. These were changed to carbonate by treatment with the carbon dioxide-containing gases from the black-ash furnace. The resulting sodium carbonate solution was concentrated to obtain crystalline sodium carbonate,<sup>2</sup> which was then dried or calcined. No LeBlanc process plant was ever built in the United States, and none is now being operated anywhere in the world. In 1861 Ernest Solvay began developing the ammonia-soda process. At first this method had great difficulty in competing with the older and well-established LeBlanc process, but in a few years the Solvay process reduced the price of soda ash almost one-third. After a struggle during which the producers of LeBlanc soda used price cutting to attempt to stifle competition, the ammonia-soda process completely displaced the LeBlanc by 1915.

The Solvay process continues to be of interest in Europe and countries without deposits of natural sodium carbonate, but by 1982, only one Solvay plant continues to operate in the

<sup>1</sup>ECT, 3d ed., vol. 1, 1978, p. 799; Hou, *Manufacture of Soda*, 2d ed., Reinhold, New York, 1942.

<sup>2</sup>A flowchart of this obsolete process is given in Badger and Baker, *Inorganic Chemical Technology*, 2d ed., McGraw-Hill, New York, 1941, p. 137.

**Table 10.1** United States Production of Soda Ash (in thousands of metric tons per year)

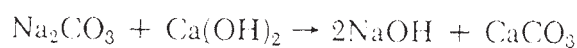
Year	Ammonia-Soda Process (Solvay)	Natural Sodium Carbonate	Total
1965	4478	1358	5836
1970	3994	2435	6429
1975	2547	3957	6504
1976	2131	4742	6873
1977	1645	5562	7207
1978		6160	
1979		7545	
1980		7540	
1981		7760	9200
1982		7500*	8690

\*Estimated.

SOURCES. *Statistical Abstract of the United States*, 101st ed.; *Chem. Eng. News*, 59 (9) 15 (1981); 60 (9) 13 (1982); and 61 (9) 25 (1983).

United States. It is kept alive by low installed cost and high freight rates. "Natural" soda from the Wyoming deposits now dominates the domestic market and has a brisk export trade as well. It requires 18.4 GJ of energy to make 1 t of soda ash by the Solvay process, but only 8.4 GJ to produce a metric ton of natural soda ash so energy costs favor mining.<sup>2a</sup> See Table 10.1 for sodium carbonate production figures.

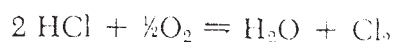
Caustic soda was originally made by batchwise causticization of LeBlanc soda (ash) with lime:



depending upon the fact that calcium carbonate is almost insoluble in caustic solution

The electrolytic production of caustic soda was known in the eighteenth century, but it was not until 1890 that caustic was actually produced in this way for industrial consumption. Until shortly before World War I, the amount of caustic soda sold as a coproduct of chlorine from the electrolytic process was almost negligible compared with that made from soda ash by lime causticization. In 1940, however, electrolytic caustic began to exceed lime-soda caustic, and by 1962 the latter had almost disappeared. Figure 10.4 shows the broad usage of caustic soda.

The first patent connected with an industrial use of chlorine is dated 1799 (a quarter century after its discovery) and was for bleaching. Chlorine was made from hydrochloric acid by the Deacon process, which does not have a satisfactory equilibrium:



The Weldon process was also used; it conducted the oxidation of HCl with expensive manganese dioxide.

<sup>2a</sup>t = 1000 kg.

Development of high-capacity direct-current electrical generating equipment toward the end of the nineteenth century made the causticization process obsolete and, by the middle of the twentieth century, more than 99 percent of the world's chlorine was produced by the electrolytic process (Table 10.2).

**USES AND ECONOMICS.** *Soda ash* is a lightweight solid, moderately soluble in water, usually containing 99.5%  $\text{Na}_2\text{CO}_3$ . It is sold on the basis of its sodium oxide content, which is generally 58%. Figure 10.1 and Table 10.3 summarize the more important uses. The production of soda ash from natural trona deposits now exceeds that from ammonia-soda. The synthetic process has been plagued by high costs and pollution problems and is disappearing in the United States.

*Pure caustic soda* is a brittle white solid that readily absorbs moisture and carbon dioxide from the air. It is sold on the basis of its  $\text{Na}_2\text{O}$  content and usually contains about 76%  $\text{Na}_2\text{O}$  equivalent to 98%  $\text{NaOH}$ . The term caustic soda is widely used because this compound is corrosive to the skin. Table 10.4 presents its diversified distribution. The traditional uses in the fields of soap, textiles, and petroleum refining are still substantial, and there is increasing use in the field of chemicals.

Since the ratio of  $\text{NaOH}$  to  $\text{Cl}_2$  manufactured is fixed by the proportions in  $\text{NaCl}$ , a difficult marketing problem constantly exists. Currently, caustic is in strong demand and expected to remain so, but during the last decade, chlorine demand has often exceeded the supply. The problems of storage of chlorine and storage or disposal costs for excess caustic have frequently made the markets very volatile.

*Chlorine*, originally used almost entirely for bleaching, has increased in importance extremely fast. This is largely due to its use in the synthesis of organic chemicals, in many of which it does not appear in the end product but enters into the intermediate steps. Table 10.2 shows the production of chlorine in the United States.

Table 10.5 reviews the consumption of chlorine. Metallurgical uses include not only the beneficiation of ores and fluxing, but also the extraction of copper, lead, nickel, gold, and platinum. The end products include such items as clothing, jewelry, paints, foods, paper, tires, and toys.

**Table 10.2** U.S. Production of Caustic Soda and Chlorine (in metric kilotons)

Year	Caustic Soda (100%) ( $\text{NaOH}$ )	Chlorine
1960	4,356	4,215
1965	6,220	5,925
1970	9,219	8,876
1975	8,454	8,334
1976	9,079	9,435
1978	10,296	10,047
1979	11,273	11,027
1980	10,600	10,450
1981	9,910	9,730
1982	8,450	8,360

SOURCE: *Chem. Eng. News*, 59 (9) 13, 14 (1981), 60 (9) 12 (1982); 61 (9) 25 (1983).

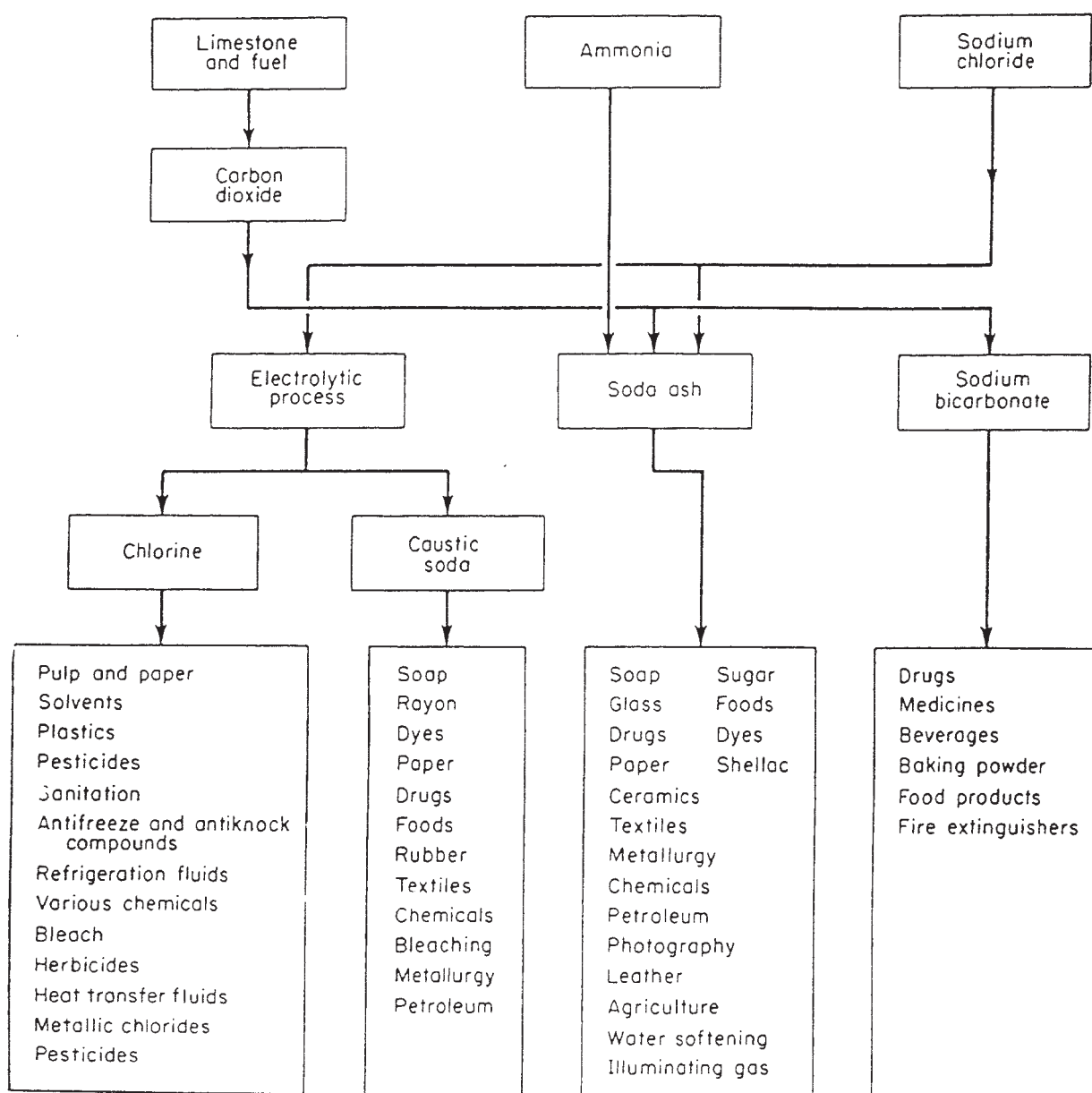


Fig. 10.1. Chlor-alkali industries chart.

**Table 10.3** Estimated Distribution of Soda Ash in the United States (for 1981)

Consuming Industry	Metric Kilotons per Year	%
Glass	4150	50
Manufacture of chemicals	1735	18
Soap and detergents	377	5
Pulp and paper	226	3
Water and sewage treatment	226	3
Miscellaneous (incl. exports)	830	21
<b>Total</b>	<b>7544</b>	<b>100</b>

SOURCE: *Chem. Week* 129 (24) 68 (1981).

**Table 10.4** Distribution of Caustic Soda Use in the United States

Consuming Industry	Metric Kilotons per Year	%
Chemical manufacturing	5,783	50
Pulp and paper	2,374	20
Cleaning products	733	6
Rayon and mercerized cotton	500	4
Oil and gas treating	570	5
Miscellaneous	1,676	15
Total	11,636	100

**Table 10.5** Distribution of Chlorine Consumption in the United States

Consuming Industry	Metric Kilotons per Year	%
Vinyl chloride	1500	17
Chloroethanes	1200	14
Pulp and paper	1100	13
Inorganic chemicals	900	10
Fluorocarbons	800	9
Propylene oxide	800	9
Miscellaneous organics	800	9
Methylene chloride	300	3
Waste water treatment	500	6
Miscellaneous	800	9
Total	8700	99

## MANUFACTURE OF SODA ASH

The Solvay process uses salt, limestone, and coke or natural gas as its raw materials and uses ammonia as a cyclic reagent. Its success depends upon the fact that ammonia, carbon dioxide, and water in the proper proportions react to form ammonium bicarbonate, which reacts with sodium chloride to form sodium bicarbonate, which is relatively insoluble in the solution used and can be filtered out and roasted to form soda ash. The ammonium chloride formed is converted back to ammonia by reaction with lime, the calcium chloride thus formed being the principal pollutant from the process. This fine old process is described in detail in the fourth edition of this book.

The Green River Basin of southwestern Wyoming is underlaid with huge deposits of trona, naturally occurring sodium sesquicarbonate ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ); some is also found in dry lakes in California. The Wyoming beds are worked by conventional underground mining techniques, although a plant using solution mining is slated to start up in 1982. Solution mining is expected to lower costs substantially, increasing exports and making the position of Solvay plants even more difficult. Very little processing of trona is required.<sup>3</sup> Solution, clari-

<sup>3</sup>Sommers, Soda Ash from Trona, *Chem. Eng. Prog.* 56 (2) 76 (1960).

fication, filtration, crystallization, drying, and calcining suffice. Depending on temperature and  $\text{CO}_2$  concentration, sesquicarbonate, sodium carbonate monohydrate, or sodium bicarbonate can be the final product. Borax-containing brines from Searles Lake<sup>4</sup> are also being processed for soda ash by a carbonation process as illustrated in Fig. 10.2. Carbonation is under a pressure of 93 KPa. Carbonation converts the carbonate present to bicarbonate, which is then flushed of brine salts, dried, and heated. This drives off  $\text{CO}_2$ , which is reused. Additional  $\text{CO}_2$  is recovered from the boiler plant flue gas by absorption with monoethanolamine solution. Bleaching with  $\text{NaNO}_3$  and high-temperature burning produces a white product. While there is a market for both light and dense sodium carbonate, the light material ( $640 \text{ kg/m}^3$ ) is ordinarily too bulky to ship economically, so a final treatment produces dense ( $993 \text{ kg/m}^3$ ) material.

## MANUFACTURE OF SODIUM BICARBONATE

Sodium bicarbonate, or baking soda, is made by treating a saturated solution of soda ash with  $\text{CO}_2$  in a contacting tower at about  $40^\circ\text{C}$ . The suspension of bicarbonate formed is removed from the bottom of the tower, filtered, and washed on a rotary drum filter. The cake is then centrifuged and dried on a continuous belt conveyor at  $70^\circ\text{C}$ . Bicarbonate made in this fashion is about 99.9% pure. Sodium bicarbonate is widely used in the food industry, in making rubber, in pharmaceuticals as an antacid, in fire extinguishers, soap and detergents, rug cleaners, animal feeds, and textiles, in leather and paper manufacturing, for flue-gas scrubbing, and for many other diversified small-scale uses. The manufacturing capacity in the United States was 250,000 t/year in 1980.

The Piceance Basin of Colorado has nahcolite (natural sodium bicarbonate) beds among

<sup>4</sup>Parkinson, Soda Ash Plant Exploits Mineral-Laden Brine, *Chem. Eng.* 84 (24) 62 (1977).

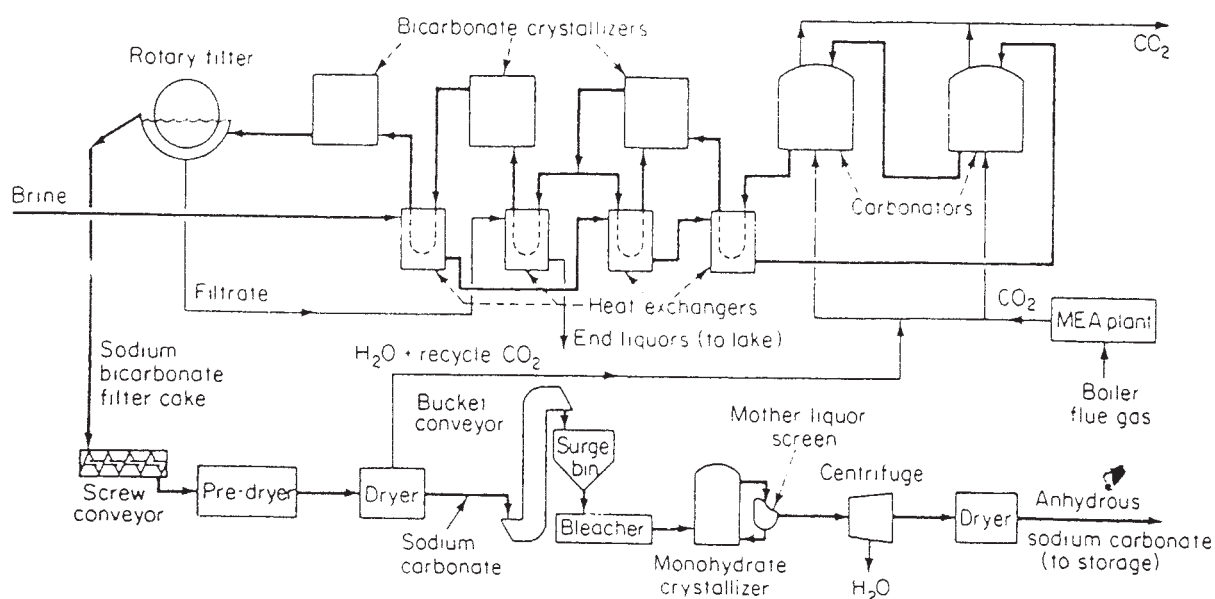


Fig. 10.2. The Kerr-McGee soda ash plant will process  $38 \text{ m}^3/\text{min}$  of brine.



the oil-shale deposits. A project is underway to recover this by underground dry mining. The crude material could be used directly for flue-gas scrubbing to remove sulfur dioxide, or as an additive for animal feed.

## MISCELLANEOUS ALKALIES

Various alkalies of different strengths are consumed commercially, according to the contained amounts of  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ , or  $\text{NaHCO}_3$ . Some of these are mechanical mixtures, such as *causticized soda ash* (soda ash with 10 to 50% caustic) for bottle washing and metal cleaning, and *modified sodas* (soda ash with 25 to 75%  $\text{NaHCO}_3$ ) for mild-alkali demands, as in the tanning industry. *Sodium sesquicarbonate*, or the natural mineral trona, is very stable and can be used without modification. It finds use in wool scouring and in laundering. *Sal soda* ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) is also known as *washing soda* or *soda crystals*. This material tends to lose water to the air on storage and to change drastically in appearance.

## MANUFACTURE OF CHLORINE AND CAUSTIC SODA

Chlorine and caustic soda are produced almost entirely by the electrolysis of aqueous solutions of alkali metal chlorides, or from fused chlorides. Brine electrolysis produces chlorine at the anode and hydrogen along with the alkali hydroxide at the cathode. If chlorine and the alkali hydroxide are to be the final product, cell design must keep them from mixing. Many ingenious designs have been invented for practical cells. At the present, three types dominate the industry, the diaphragm cell, the membrane cell, and the mercury cell. There are many variations of each type.

### REACTIONS AND ENERGY CHANGES

**Decomposition Voltage and Voltage Efficiency.** The energy consumed in the electrolysis of the brine is the product of the current flowing and the potential of the cell. The theoretical, or minimum, voltage required for the process may be derived from the Gibbs-Helmholtz equation, which expresses the relation between the electric energy and the heat of reaction of a system.<sup>5</sup>

$$E = \frac{-J\Delta H}{nF} + \frac{T dE}{dT}$$

where  $E$  = theoretical decomposition voltage

$\Delta H$  = enthalpy change of reaction

$J$  = electrical equivalent of heat

$T$  = absolute temperature

$F$  = Faraday constant

$n$  = number of equivalents involved

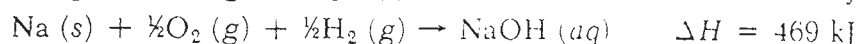
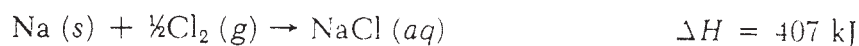
†

<sup>5</sup>Perry, 5th ed., p. 4.

The heat of reaction for the electrolysis of salt may be found from the heats of formation of the components of the overall reaction, which is:



This may be broken down to the following reactions for formation:

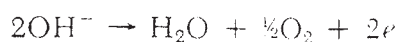


The net  $\Delta H$  for the overall reaction results from

$$+407 + 286 - 469 = 224 \text{ kJ}$$

When this value of  $\Delta H$  is substituted in the Gibbs-Helmholz equation and the change in voltage with temperature is neglected, the value of  $E$  is found to be 2.31 V. The omission of  $T dE/dT$  involves an error of less than 10 percent for most cells.

The ratio of this theoretical voltage to that actually used is the *voltage efficiency* of the cell. Voltage efficiencies range from 60 to 75 percent. According to Faraday's law, 96,500 C of electricity passing through a cell produce 1 gram-equivalent of chemical reaction at each electrode. Because of side reactions, cells usually require more than this amount. The ratio of the theoretical to the actual current consumed is defined as the *current efficiency*. Current efficiencies run 95 to 97 percent and, unless otherwise specified, are understood to be *cathode current efficiencies*. The current divided by the area on which the current acts is known as the *current density*. A high value is desirable. The product of voltage efficiency and current efficiency is the *energy efficiency* of the cell. Another consideration is the *decomposition efficiency*, which is the ratio of equivalents produced in the cell to equivalents charged. In the usual commercial cell, this decomposition efficiency is about 60 to 65 percent. Some newer, larger membrane cells claim efficiencies as high as 75 to 80 percent. Diaphragm cells operated to obtain very high decomposition efficiencies encounter difficulties with the migration of hydroxyl ions back to the anode, resulting in the formation of hypochlorite ion. Hydroxyl ions are decomposed on the anode by the reaction:



The oxygen formed reacts with the graphite of the anodes, causing decreased anode life. In cells with metal anodes, the oxygen does not react.

**CELL TYPES.** Only a few years ago, it seemed that the mercury cell would soon dominate the field because of the high quality of its product and the reduced evaporation required, but unexpected difficulties arose. Mercury discharge into nearby waters, although small in quantity, was found to be the source of methyl mercury, which caused a particularly debilitating disease first observed in Japanese children. This connection led to drastic reductions in the permissible discharge of mercury into either air or water, and now has led some countries to prohibit production with mercury cells entirely. Improved designs of membrane cells and newer and cheaper purification techniques have reduced costs and improved efficiencies to the point that the membrane cell with dimensionally stable titanium anodes now appears to be about to dominate the field. In this slow-growing business, changes will come about slowly.



In 1979, 50 percent of world production<sup>6</sup> was by mercury cells and 49 percent by diaphragm cells. In the United States 74.3 percent of the plants used diaphragm cells and 20.3 percent mercury cells. In Japan, where mercury cells must be totally replaced by 1984, membrane cells will most certainly be the technique of choice.

Nothing stimulates process improvement like competition so severe that existence is threatened, thus mercury and diaphragm cells will probably be quickly improved and should be around for a long time.

### ***Diaphragm Cells***

Diaphragm cells contain a diaphragm, usually made of asbestos fibers, to separate the anode from the cathode. This allows ions to pass through by electrical migration but reduces the diffusion of products. Anodes have usually been made of graphite, cathodes of cast iron. Diaphragms permit the construction of compact cells of lowered resistance because the electrodes can be placed close together. The diaphragms become clogged with use, as indicated by higher voltage drop and higher hydrostatic pressure on the brine feed. They must be replaced regularly. The diaphragm permits a flow of brine from anode to cathode and thus greatly lessens or prevents side reactions (e.g., sodium hypochlorite formation). Cells with metal cathodes (titanium coated with rare earth oxides, platinum or noble metals, or oxides) rarely develop clogged diaphragms and operate for 12 to 24 months without requiring diaphragm replacements. It is expected that diaphragms made of corrosion-resistant plastics will increase service life and remove the environmentalist's objection to any process that may release asbestos fibers into the environment. Figure 10.3 shows a modern monopolar diaphragm cell, and Fig. 10.4 a cell room.

<sup>6</sup>Savage, *Chem. Eng.* 86 (24) 63 (1979).

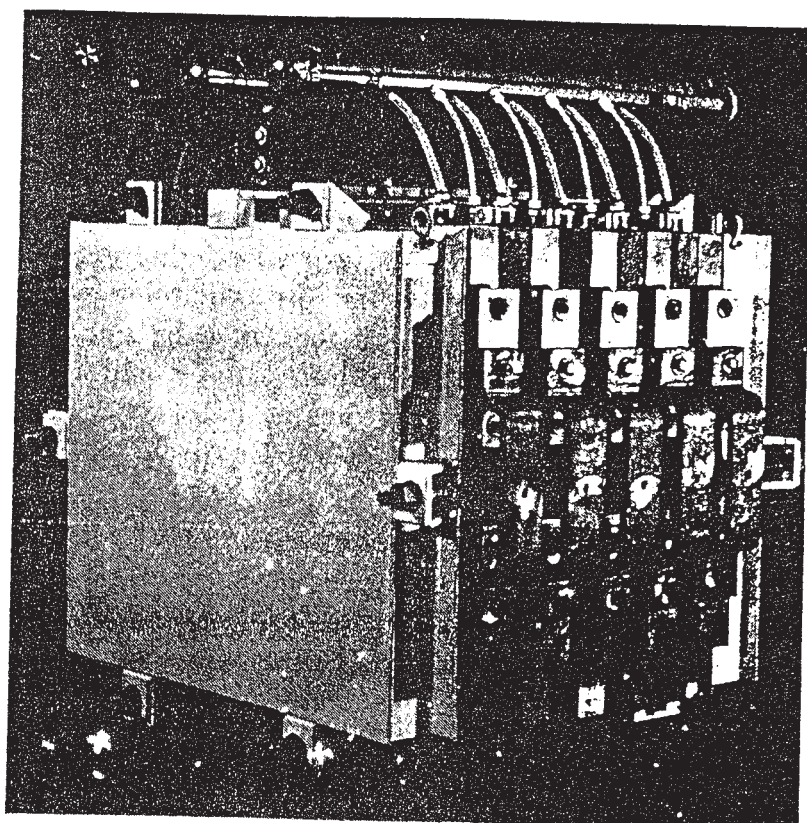


Fig. 10.3. Monopolar caustic-chlorine cell. (Courtesy of Diamond Shamrock Corp.)

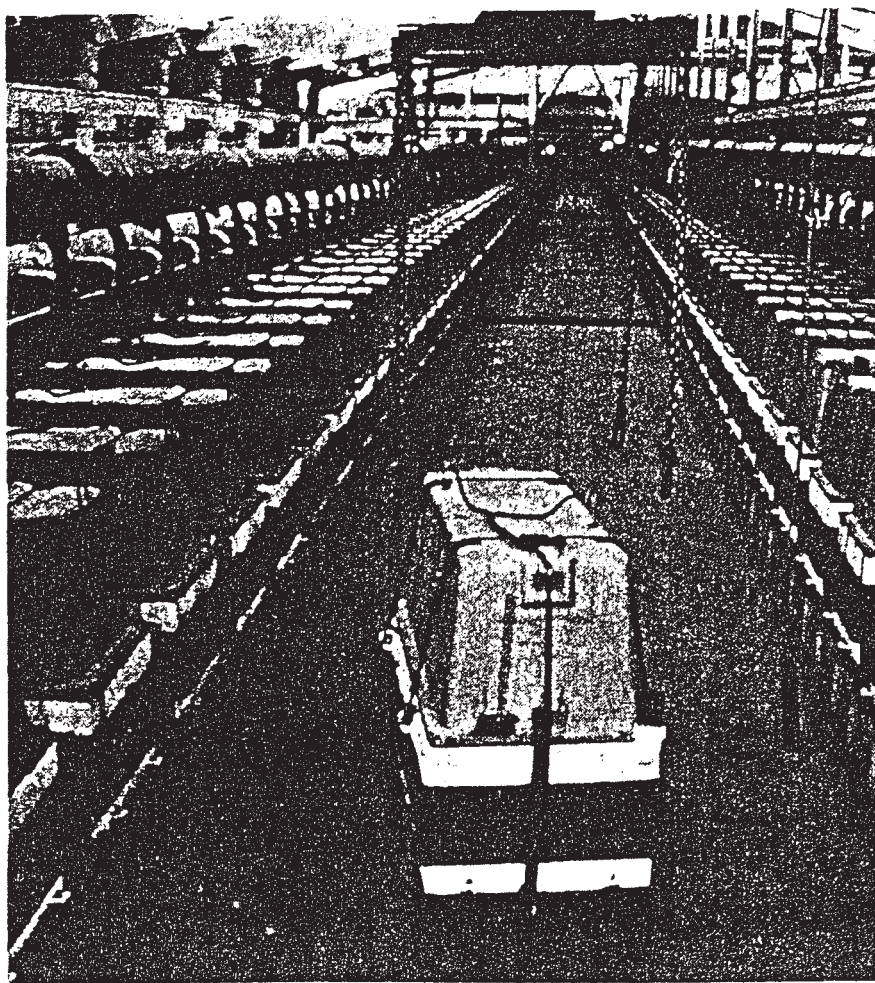


Fig. 10.4. Caustic-chlorine diaphragm cell room. (Courtesy of Diamond Shamrock Corp.)

A major advantage of the diaphragm cell is that it can run on dilute (20%), fairly impure brine. Such dilute brines produce dilute sodium hydroxide (typically 11% NaOH with 15% NaCl) contaminated with sodium chloride as a product. Concentration to the usual shipping strength of 50% is required, and this consumes a great deal of energy even when multiple-effect evaporators are used. Approximately 2600 kg of water must be evaporated to produce a ton of 50% caustic. Although salt is not very soluble in concentrated caustic solution, the small amount of chloride ion which remains is highly objectionable to some industries (e.g., rayon manufacture). Sodium chlorate is also objectionable when caustic is to be used in the manufacture of glycerin, pentaerythritol, sodium sulfate, sodium hydrosulfate, cellophane, and several other chemicals. A catalytic reduction<sup>7</sup> with hydrogen can remove this without resorting to ammonia extraction.

### Membrane Cells

Membrane cells use a semipermeable membrane to separate the anode and cathode compartments. With diaphragm cells, back migration of ions is controlled by the rate of flow of

<sup>7</sup>Mitchell and Modan, Catalytic Purification of Diaphragm Cell Caustic, *Chem. Eng.* 86 (5) 88 (1979).

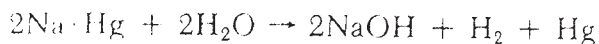
fluid through the diaphragm, and this is regulated by careful control of liquid levels in the compartments. Membrane cells<sup>8</sup> separate the compartments with porous chemically active plastic sheets that allow sodium ions to pass but reject hydroxyl ions. Several polymers have been developed for this demanding service. DuPont has developed a perfluorosulfonic acid polymer (Nafion), while Ashai uses a multiple-layer membrane of perfluorosulfonic acid polymer coated on one side with a perfluorocarboxylic acid polymer. The purpose of the membrane is to exclude  $\text{OH}^-$  and  $\text{Cl}^-$  ions from the anode chamber, thus making the product far lower in salt than that from a diaphragm cell. Membrane cells operate using a more concentrated brine and produce a purer, more concentrated product (28% NaOH containing 50 ppm of NaCl; 40% NaOH product has recently been claimed<sup>9</sup>). Such product requires only 715 kg of water to be evaporated to produce a metric ton of 50% caustic; a considerable saving. Because of the difficulty and expense of concentration and purification, only large diaphragm cell installations are feasible. Membrane cells, producing relatively concentrated NaOH offer the possibility of operation at the point of caustic use, thus saving freight. Small, efficient units may cause a revolution in the distribution of the chlor-alkali industry, particularly if efficiencies remain high in small units. No commercial-sized membrane units were operating in the United States in 1982.

Serious suggestions have been made<sup>10</sup> that a combination plant using the output of the membrane cells as feed to the diaphragm cells might result in the optimum application of both and make a considerable cost reduction overall. Such combinations have been used with mercury cell output feeding diaphragm cells. Membranes are more readily clogged than diaphragms, so some of the savings are lost because of the necessity to pretreat the brine fed in order to remove calcium and magnesium before the electrolysis.

A membrane cell 20 times larger than former cells is being offered (1981).<sup>11</sup> Such a cell unit can produce 240 t of chlorine per year, and power consumption is substantially reduced below either mercury or diaphragm cells. A bipolar cell unit is capable of producing 20,000 t/year with a current density of 4 kA/m<sup>2</sup>.

## Mercury Cells

Mercury cells operate quite differently from the other types. The anodes remain either graphite or modified titanium as before, but the cathode is a flowing pool of mercury. The electrolysis produces a mercury-sodium alloy (amalgam) which is not decomposed by the brine present. The amalgam is decomposed in a separate vessel according to the reaction:



When exactly the correct amount of water is used, 50% NaOH with a very low salt content (30 ppm) becomes the direct product with no evaporation required. The small loss of mercury to the environment presents extreme problems.

Japan outlawed mercury cell use after 1975 (later extended to 1984). Although major reductions in the mercury discharged had taken place, the construction of mercury cells in

<sup>8</sup>Chlor-alkali Membrane Cell Set for Market, *Chem. Eng. News* 56 (12) 20 (1978).

<sup>9</sup>Ukihashi, A Membrane for Electrolysis, *CHEMTECH* 10 (2) 118 (1980).

<sup>10</sup>Savage, Membrane Cells a Hit with Chlorine Producers, *Chem. Eng.* 86 (24) 63 (1979).

<sup>11</sup>*Chem. Week*, 130 (6) 50 (1982).

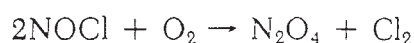


the United States came to an abrupt halt. Careful process control, combined with treatment of water and air effluent, may make it possible for mercury plants to meet environmental standards and survive, but most companies are hesitant to erect new units. Diaphragm cells and membrane cells use about the same amount of electrical energy, mercury cells somewhat more. The ratio is approximately 3:4.

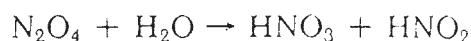
**HYBRID FUEL CELLS.** The hydrogen from any type of cell can be reacted in an efficient fuel cell to produce a significant amount of electrical energy. If this energy is used for electrolysis, costs should be reduced around 20 percent. This development is expected to take place during the next decade.

### Other Processes

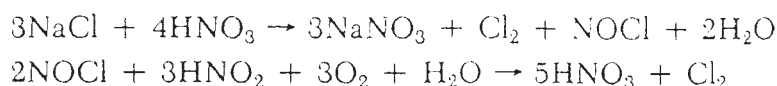
Other processes for making chlorine include the Downs cell (for making sodium, Chap. 11), caustic potash manufacture, hydrogen chloride decomposition (Chap. 11), the nitrosyl chloride process, and the process where salt is treated with nitric acid to form sodium nitrate and chlorine with nitrosyl chloride (containing 4 to 10% nitrogen tetroxide) as a by-product. The nitrosyl chloride vapor is placed in contact with oxygen to produce nitrogen tetroxide and chlorine:



After liquefying and distilling the chlorine out, the nitrogen tetroxide is absorbed in water to make nitric acid and nitrous acids, which are recycled:



The advantage of this process is that it produces chlorine but no caustic soda. The limited demand for sodium nitrate regulates the amount of chlorine that can be made in this way. The overall reactions may be simplified as follows:



DuPont has started up a 550 t/day plant to recover chlorine from hydrogen chloride by the Kel-Chlor<sup>12</sup> process. This process accepts either gaseous or aqueous hydrogen chloride and converts it to chlorine, using a four-step operation based on the Deacon process but involving nitrosyl sulfuric acid (NHSO<sub>5</sub>) as a catalyst. The development of oxychlorination technology has been the major factor in reducing the oversupply of by-product hydrogen chloride from organic chlorination processes.

Another thermal process<sup>13</sup> designed to produce chlorine from chloride salts without electrolysis reacts sodium chloride with sulfuric acid, then reacts the hydrogen chloride with oxy-

<sup>12</sup>Hydrogen Chloride to Chlorine via the Kel-Chlor Process *Chem. Eng.* 69 (4) 57 (1974); The Kel-Chlor Process, *Ind. Eng. Chem.* 61 (7) 23 (1969).

<sup>13</sup>*Chem. Eng.* 88 (22) 25 (1981).

gen over a mixed  $K_2SO_4$ - $V_2O_5$  catalyst to form chlorine. Only bench-scale work has been completed. Because of the expected stronger demand for caustic than chlorine, these processes are currently of small interest, but the situation may well change with time.

## **UNIT OPERATIONS AND CHEMICAL CONVERSIONS**

**BRINE PURIFICATION.** Calcium, iron, and magnesium compounds all tend to plug diaphragms. Precipitation with soda ash and caustic soda is commonly practiced. Additional treatment with phosphates and as yet undisclosed other substances is required for membrane cells. Sulfates may be removed by treatment with barium chloride. Brine is preheated against other streams to reduce energy requirement.

**BRINE ELECTROLYSIS.** Whatever type of cell is used, 3.0 to 4.5 V per cell are required. When cells are connected in parallel and low voltage is provided to each cell, the connection is known as monopolar. When cells are connected in series, allowing generation and use of power at higher voltages, the cell is said to be bipolar. Smaller bus bars are required for bipolar systems.

**EVAPORATION AND SALT SEPARATION.** Diaphragm cells discharge a brine containing around 11% NaOH and 15% NaCl. On concentration to 50% NaOH in multiple-effect nickel-tubed evaporators, most of the salt crystallizes out and can be removed for recycling. Where the presence of 1% salt is not objectionable, this 50% solution is shipped as a standard commercial strength. Concentration to 73% caustic solution reduces the shipping cost, but greatly increases the shipping and unloading problem because the high melting point of the concentrated material makes steam-heated lines and steam heating of the tank cars necessary. The melting points are: for 50%, 12°C; for 73%, 65°C.

Membrane cells produce caustic that is much more concentrated than that from diaphragm cells (28 to 40%) and that contains very little chlorine, so less evaporation or treatment is required.

No evaporation is required to produce a 50% solution when mercury cells are used.

**FINAL EVAPORATION.** Either the cooled and settled 50% caustic or a specially purified caustic may be concentrated in a single-effect final or high evaporator to 70 to 75% NaOH, using steam at 500 to 600 kPa. This very strong caustic must be handled in steam-traced pipes to prevent solidification. It is run to the finishing pots. Another method of dehydrating 50% caustic utilizes the precipitation of NaOH monohydrate. This monohydrate contains less water than the original solution. Precipitation is accomplished by the addition of ammonia to the 50% solution, and this also purifies the caustic. If the 50% solution is treated with anhydrous ammonia,<sup>14</sup> particularly in a countercurrent system, free-flowing anhydrous crystals separate from the resulting aqueous ammonia. This procedure must be carried out in pressure vessels.

**FINISHING OF CAUSTIC IN POTS.** Although 50% caustic was at one time finished in special close-grained, cast-iron, direct-fired pots, the heat efficiency is so low that good practice now

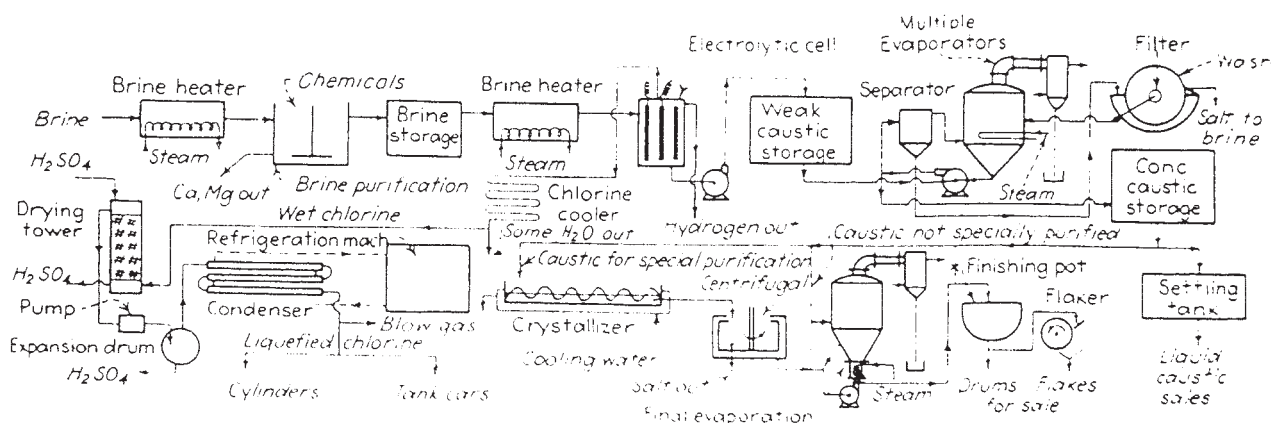
<sup>14</sup>Muskat, Method for Producing Anhydrous Caustic, U.S. Patent 2,196,593 (1940)

handles only 70 to 75% NaOH in this fashion. The final temperature is 500 to 600°C and boils off all but about 1% or less water. These pots are now being replaced by Dowtherm heated evaporators, even above 50%. The hot anhydrous caustic is treated with sulfur to precipitate iron and settled. The product is pumped out by a centrifugal pump that discharges the molten material into thin steel drums holding about 320 kg, or into a flaking machine. Some caustic is made into beads, which some think handle more readily than flakes. All types of solid caustic are more expensive (about 50%) than solutions and have but a small amount of the total market. Much of the solid manufactured goes to exports, because the saving in shipping cost is important.

**SPECIAL PURIFICATION OF CAUSTIC.** Some of the troublesome impurities in 50% caustic are colloidal iron, NaCl, and NaClO<sub>3</sub>. The iron is often removed by treating the caustic with 1% by weight of finely divided calcium carbonate and filtering the resulting mixture through a Vallez filter on a calcium carbonate precoat. The chloride and chlorate may be removed by allowing the 50% caustic to drop through a column of 50% aqueous ammonia solution. This treatment produces caustic almost as free of chlorides and chlorates as that made by the mercury process. To reduce the salt content of the caustic necessary for certain uses, it is cooled to 20°C in equipment such as that outlined in Fig. 10.5. Another crystallization method used industrially, however, involves the actual separation of the compound NaOH · 3½H<sub>2</sub>O or NaOH · 2H<sub>2</sub>O, leaving the NaCl in the mother liquor. Another procedure reduces the salt content of the caustic soda solution by formation of the slightly soluble complex salt NaCl · Na<sub>2</sub>SO<sub>4</sub> · NaOH.

A standard process for the continuous extraction of NaCl and NaClO<sub>3</sub> in 50% caustic solution is countercurrent extraction in vertical columns with 70 to 95% ammonia. Mercury cells furnish caustic soda essentially free from salt. These purification or manufacturing methods give high grade caustic with less than 1% impurities (anhydrous basis).

**CHLORINE DRYING.** The hot chlorine evolved from the anode carries much water vapor. It is first cooled to condense most of this vapor and then dried with sulfuric acid in a scrubber



In order to produce 1 t 76% caustic, 879 kg chlorine, and 274.7 m<sup>3</sup> hydrogen (25.2 kg H<sub>2</sub>), the following materials and utilities are required:

Salt	1.6 t	Electricity	1197 kJ
Sodium carbonate	29.2 kg	Refrigeration	0.91 t
Sulfuric acid (66°Bé)	100.5 kg	Direct labor	20 work-h
Steam	10.060 kg		

\*Daily production is 75.4 t caustic.

Fig. 10.5. Flowchart for the purification of caustic soda and chlorine using a diaphragm cell.



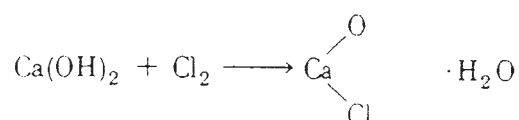
or tower, as shown in Fig. 10.5. Up to the sulfuric acid tower, the wet chlorine should be handled in polyester, polyvinyl chloride, or similar resistant material; after drying, iron or steel can be employed.

**CHLORINE COMPRESSION AND LIQUEFACTION.**<sup>15</sup> The dried chlorine is compressed to 240 kPa, or sometimes 550 kPa. For lower pressures, the usual type of compressor employed is the liquid-piston rotary compressor constructed of iron, with concentrated sulfuric acid as the sealing liquid. For larger capacities and higher pressures, centrifugal and nonlubricated reciprocating compressors are chosen. Carbon piston rings or carbon cylinder liners are usually used in the reciprocating compressors, other parts being of cast iron. The heat of compression is removed and the gas condensed. The liquid chlorine is stored in small cylinders, ton cylinders, pipeline, or the 50-t tank cars that are shipped to large consumers. Barges carrying 550 or 1000 t are also employed. There is always some residue, or "blow gas," made up of an equilibrium mixture of chlorine and air. The blow gas is used to make chlorine derivatives, either organic or inorganic, especially bleaching powder.

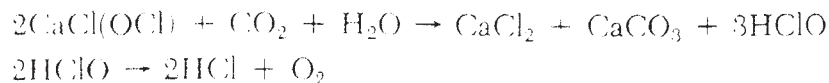
**HYDROGEN DISPOSAL.** The hydrogen is frequently made into other compounds, such as hydrochloric acid or ammonia, or is employed for the hydrogenation of organic compounds. It may also be burned for heat generation or used in a fuel cell to produce electricity.

## BLEACHING POWDER

A decreasing tonnage of chlorine gas goes into the production of bleaching powder, chiefly because of its instability and the large proportion of inert material. The reaction by which bleaching powder is made is



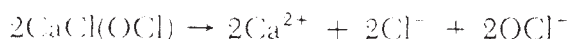
This reaction is carried out below 50°C in a countercurrent fashion by passing chlorine through a rotating steel cylinder with inner lifting blades which shower the solid through the path of the gas. When allowed to stand in the air, the bleaching powder absorbs carbon dioxide. Other inorganic acids will also liberate the HOCl.



Simply on standing, however, the following decomposition takes place:



When dissolved in water, the reaction gives ionized calcium chloride and hypochlorite



<sup>15</sup>Eichenhofer and Fedoroff, Chlorine Liquefaction, *Chem. Eng.* 58 (12) 142 (1951)