

# Handbook of Chlorination

### For my wife Charlotte

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## **Preface**

In preparing this book, I have attempted the monumental task of bringing together under one cover all the pertinent information necessary to provide a practical "real world" approach to the entire subject of chlorination as it is applied to potable water, wastewater, cooling water, industrial water, and swimming pools.

Several factors inspired me to write this book. First and foremost was the fact that to my knowledge such a book had never been written. The quest for information on this subject has grown rapidly, particularly by the water and wastewater industries. Whenever I gave a lecture or held a seminar on the subject I was usually asked if a reference text were available. This, coupled with the rising interest and demands for water pollution abatement seemed reason enough for such a text to be made available. I hoped that my thirty-five years of active participation in the field of chlorination could be turned into a significant contribution to the environmental sciences.

The first step in this project was to make a systematic review of the literature. This took well over a year, and fortunately I had at my disposal a fine array of scientific libraries in the San Francisco Bay area. I read and studied some thousand or more references scattered through upward of fifty different scientific periodicals. Whenever I was unable to resolve the contents of a particular reference, and this did occur several times, I corresponded with the author for amplification or explanation. This proved most valuable, as all the authors were most co-operative.

In addition to the above reference material, I have collected for my own use over the years a vast amount of information of great practical value derived from personal experience in all the various applications of chlorine in the United States, Canada, Great Britain, and the European continent. Some is from private communications with colleagues here and abroad. A great deal of the information contained in this book has never been published before to my knowledge.

It is intended that this book be a handbook for the designer, a manual for the operator, a textbook for the student, and a guide for the regulatory agencies. I have tried to present this information so that anyone with a background of high school chemistry and mathematics will have no difficulty in understanding the text.

The reader will note that in some instances, particularly in Chapter 10, the references are listed without page numbers. This means that I worked from my collection of reprinted articles which do not show the page numbers as they appear in the periodicals.

Producing this book has been a formidable but enjoyable task, and I am most appreciative of the help I have had along the way from my colleagues. I hope this work will please them.

San Francisco G.C.W.

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# History, Manufacture, and Properties of Chlorine

Chlorine is an element of the halogen family, but it is never found uncombined in nature. It is estimated to account for 0.15 percent of the earth's crust in the form of soluble chlorides, such as common salt (NaCl), carnallite (KMgCl<sub>3</sub> ·  $6H_2O$ ), and sylvite (KCl). In nature, therefore, it exists only as the negative chloride ion with a valence of -1.

Chlorine is a most unusual and versatile chemical, since its properties differ so widely in the gaseous, liquid, and aqueous states. For this reason, each phase will be treated separately.

### **CHLORINE GAS**

Chlorine was discovered in its gaseous state in 1774 by Karl W. Scheele, a Swedish chemist, when he heated a black oxide of manganese with hydrochloric acid:1

$$MnO_2 + 4HCl \xrightarrow{heat} MnCl_2 + Cl_2 + 2H_2O$$
 (1-1)

The chlorine thus liberated is a strong-smelling, greenish-yellow gas with a pungent odor; it is extremely irritating to mucous membranes.

This element must certainly have been known to the medieval Arab chemist Geber (ca. 720-810), as he was the discoverer of aqua regia (3 parts HCl, 1 part HNO<sub>3</sub>), used to dissolve the noble metals. When this mixture is heated, it gives off fumes similar to "Scheele's gas," about which there was a great controversy when it was studied by the great chemists Berthollet, Lavoisier, Gay-Lussac, Berzelius, Therrard, and Davy.<sup>1</sup>

Scheele called the gas he discovered dephlogisticated muriatic acid on the theory that manganese had displaced phlogiston (as hydrogen was then called) from the

muriatic acid (HCl). Scheele also observed that the gas was soluble in water, that it had a permanent bleaching effect on paper, vegetables, and flowers, and that it acted on metals and oxides of metals.

During the decade following Scheele's discovery, Lavoisier successfully attacked and, after a memorable struggle, completely upset the phlogiston theory of Scheele. Lavoisier was of the opinion that all acids contained oxygen. Berthollet found that a solution of Scheele's gas in water, when exposed to sunlight, gives off oxygen and leaves muriatic acid behind. Considering this residue proof of Lavoisier's theory, Berthollet called it oxygenated muriatic acid.<sup>2</sup> However, Humphry Davy (1778-1829) was unable to decompose Scheele's gas. On July 12, 1810, before the Royal Society of London, he declared the gas to be an element, which in muriatic acid is combined with hydrogen. Therefore, Lavoisier's theory that all acids contain oxygen had to be discarded, Davy proposed the name "chlorine" from the Greek "chloros," variously translated "green," "greenish yellow," or "yellowish green," in allusion to the color of the gas.<sup>1</sup>

Pelletier in 1785 and Karsten in 1786 succeeded in forming yellow crystals of chlorine hydrate by cooling Scheele's gas in the presence of moisture. From this they inferred that it was not an element. In 1810, Davy proved that these crystals could not be formed by cooling the gas even to  $-40^{\circ}$ F in the absence of moisture. It is now known that these crystals are in fact chlorine hydrate (Cl<sub>2</sub> · 8H<sub>2</sub>O) and will form under standard conditions with chlorine gas in the presence of moisture beginning at  $49.3^{\circ}$ F.

### CHLORINE LIQUID

In 1805, Thomas Northmore liquefied Scheele's gas by compression. He noted that it became a yellowish amber liquid under pressure and, upon release of the pressure, volatilized rapidly and violently into a green gas. He further noted its pungent odor and severe damage to machinery.

Michael Faraday (1791-1867) also observed liquid chlorine. On March 5, 1823, he was visited in his laboratory (he worked as an assistant to Davy) by J. A. Paris while he was working with chlorine hydrate in a sealed tube. Paris noted a yellowish, oily-appearing substance in the tube and chided Faraday for working with dirty apparatus. When Faraday tried to open the tube, it shattered and the oily substance vanished. After studying the accident, Faraday wrote Paris: "Dear Sir: The oil you saw in the sealed tube yesterday turned out to be liquid chlorine. Yours faithfully, Michael Faraday."

### MANUFACTURE OF CHLORINE

From 1805 to 1888, Scheele's gas remained a laboratory curiosity — and a dangerous one — until it was produced on a commercial scale by cooling and compression in a suitable apparatus. This was made possible by Kneitsch's discovery in 1888 that dry chlorine did not attack iron or steel, thus making it possible to package chlorine as a liquid under pressure.

Until this time, chlorine was used as a bleaching agent in the form of a solution. In 1785, Berthollet prepared this solution by dissolving Scheele's gas in water and adding it to a solution of caustic potash. This was done at a chemical plant in Javel, then a small French town, now a part of Paris. Hence, the solution is known as Javelle water. James Watt, the inventor, obtained from Berthollet a license for the manufacture of Javelle water and brought it to Scotland for Charles Tennant, founder of the English chemical company. In 1789, Tennant, through extensive experimentation, produced another liquid bleaching compound, a chlorinated milk of lime. A year later, he improved it greatly by making it a dry compound, which has been known ever since as bleaching powder. The chlorine for the manufacture of bleaching powder was obtained by Berthollet's method of heating sodium chloride, manganese, and sulfuric acid in lead stills. During this time, chlorine was also being made on a limited scale by the Weldon process, which employed the basic reaction of Scheele's discovery, hydrochloric acid and manganese dioxide. This method was given considerable impetus when in 1836 Gossage invented his coke towers for the absorption of waste hydrochloric acid, resulting from the LeBlanc soda process. This invention resulted in cheap hydrochloric acid for the Weldon process. However, in 1868, Scheele's method by the Weldon process became obsolete.\* Henry Deacon and Ferdinand Hurter patented a process for producing chlorine by decomposing hydrochloric acid with atmospheric oxygen in the presence of a catalyst.<sup>2</sup> A mixture of hydrochloric acid and air is heated. About 70 percent of the hydrogen chloride can be converted to chlorine as it mixes with the air and steam. This mixture is condensed, and the steam absorbs the hydrogen chloride, forming a very strong muriatic acid mixed with hydrogen chloride gas. This mixture is passed through a superheater, raised to about 430°C, and then passed through a decomposer consisting of a brick- or pumice-lined chamber impregnated with cupric chloride, the catalyst. After this step, the mixture is washed first with water and then with sulfuric acid. The remaining mixture consists of nitrogen and oxygen containing 10 percent chlorine gas, which can be utilized without any difficulty in the manufacture of bleach liquids and powders. The original HCl is recycled so that the only additional materials are heat and air. Considering the amount of chlorine produced, the plant is extremely bulky. The reaction employed is:

$$4HCl + O_2 \xrightarrow{\text{heat}} + \xrightarrow{\text{catalyst}} 2Cl_2 + H_2O$$
 (1-2)

This reaction is reversible and incomplete. The rate of reaction is made satisfactory by the addition of heat and the catalyst, cupric copper.

The hydrogen chloride in this process is largely a by-product of the LeBlanc soda process. With the advent of the Solvay sodium ammonia process in 1870, the LeBlanc process fell into a sharp decline, causing the abandonment of the Deacon process in favor of the electrolytic methods which were then emerging from the experimental state.

<sup>\*</sup> The Weldon process or Scheele's method is still used to advantage for making hypochlorites in remote areas. (See Chapter 12.)

### **Electrolytic Processes**

In 1883, after years of research, Faraday postulated the laws that govern the action of passing an electric current through an aqueous salt solution. He coined the word "electrolysis" to describe the resulting phenomenon. These fundamental laws are among the most exact in chemistry and are as follows:

The weight of a given element liberated at an electrode is directly proportional to the quantity of electricity passed through the solution. (The unit of electrical quantity is the coulomb.)

The weights of different elements liberated by the same quantity of electricity are proportional to the equivalent weights of the elements.

Charles Watt obtained an English patent for the electrolytic manufacture of chlorine in 1851. However, at that time electric current generators of sufficient size were not available, and so the patent was only of academic interest. When this equipment became available, interest in electrochemistry was greatly stimulated. In 1890 the first commercial production of chlorine by the electrolytic method was introduced by the Elektron Company (now Farbwerke-Hoechst A.G.) of Griesheim, West Germany. The first electrolytic plant to go into production in America was at Rumford Falls, Maine, in 1892 for the Oxford Paper Company. In 1894, Mathieson Chemical Company acquired the rights to the Castner mercury cell and began the first commercial production of bleaching powder at a demonstration plant in Saltville, Virginia. In 1897, this operation was moved to Niagara Falls, New York. These original Castner rocking cells operated successfully until they were shut down in 1960.<sup>3</sup>

At first, the electrolytic process for the commercial production of chlorine was primarily for the manufacture of caustic. Chlorine was a by-product. At the Niagara Falls plant, a small amount was used for bleach and for the making of hydrochloric acid, the rest being discharged into the Niagara River. Not until 1909 was liquid chlorine manufactured on a commercial basis. It was first packaged in 100-lb capacity steel cylinders made in Germany. The business grew slowly but steadily, most consumers using it for bleaching textiles, pulp, and paper. The first American tank car, with a capacity of 15 tons, was manufactured in 1909. The next year 150-lb cylinders came into use, and in 1917 ton containers were made for the chemical warfare service.

Chlorine is now manufactured from the electrolysis of brine by two different methods — diaphragm cells, and mercury cells. Other methods of chlorine production include the electrolysis of hydrochloric acid, the salt process, and the HCl oxidation processes.

In the methods utilizing the electrolysis of brine, chlorine comes off as a hot gas at the graphite anode, and hydrogen comes off at the cathode together with a coproduct, caustic, resulting from the electrolysis of the brine solution. The diaphragm cell separates the anolyte from the catholyte by an asbestos diaphragm amounting to a deposit of an asbestos slurry on a steel screen that is the cathode. In the mercury cell, no such separation is required as the cathode becomes a flowing

mercury amalgam of sodium. The latter is a result of electrolytic decomposition of the brine. The diaphragm cell can produce the coproduct caustic at only 11 to 12 percent strength, while the mercury cell produces caustic at 50 percent strength.<sup>4</sup>

The estimated total United States chlorine production for 1970, including pulp and paper mills, is 28,276 tons per day. Of this amount, 69.2 percent is produced by diaphragm cells, 27.6 percent by mercury cells, and 3.2 percent by fused salt and nonelectrolytic processes.<sup>5</sup> The latter processes include the HCl oxidation process and the HCl catalytic oxidation process, each of which is an improvement over the long-abandoned Deacon process. The Deacon process has recently been revived because the need for chlorine has increased at a faster rate than that for caustic soda (a by-product of the electrolytic process). This has created a demand for chlorine production from by-product HCl as well as from metal chlorides.

Electrolysis of Brines in Diaphragm Cells Chlorine manufactured by diaphragm cells accounts for approximately 70 percent of the total United States production. <sup>5</sup> Although several hundred types of diaphragm cells have been designed, those most widely used are of two basic types: the Stuart, patented by Hooker Electro-Chemical Company; and the Dow. The Stuart (Hooker) type includes the Columbia-Hooker cells and the Diamond-Alkali cells; the Dow bipolar filter press cell includes the Hunter-Otis-Blue and the Lucas-Armstrong designs. Both types have vertical graphite anodes, steel screen cathodes, and deposited asbestos diaphragms. The major differences in these two types and designs are in the way they are assembled and in the method of introducing the chemicals and of withdrawing the products of electrolysis.

In Figs. 1-1 and 1-2, the following chemistry is involved:

The overall chemical reaction is

$$2 \text{ NaCl} + \text{H}_2 \text{ O} + \text{electric current} \longrightarrow 2 \text{NaOH} + \text{Cl}_2 + \text{H}_2$$
 (1-3)

The principal anode reaction is:

$$2Cl^{-} \longrightarrow Cl_2 \uparrow + 2e \tag{1-4}$$

Chlorine formed at the anode saturates the anolyte, and an equilibrium is established, as follows:

$$Cl_2 + OH^- \longrightarrow Cl^- + HOCl$$
 (1-5)

$$HOCl \longrightarrow H^+ + OCl^-$$
 (1-6)

The principal cathode reaction is:

$$2H^+ + 2OH^- \longrightarrow H_2 \uparrow + 2OH^- + 2e \tag{1-7}$$

Therefore the  $H^+$  ion present as  $H_2O$  in the catholyte evolves at the cathode as hydrogen gas, leaving the hydroxyl ion  $(OH^-)$  behind in the catholyte. Since chlorine has evolved at the anode, the sodium ion is free to join the hydroxyl ion as it migrates from the anolyte chamber to the catholyte chamber by means of a

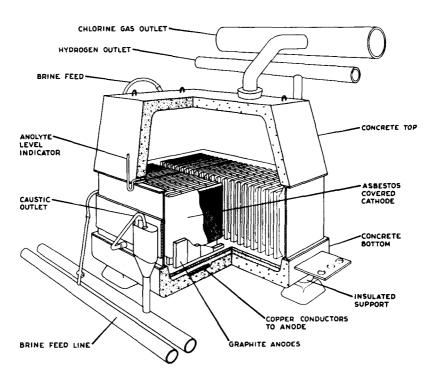


Fig. 1-1. Hooker type S-4 diaphragm cell. Courtesy Hooker Chemical Company.

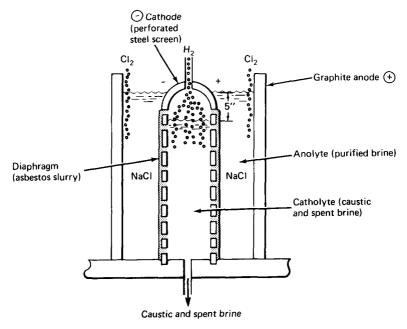


Fig. 1-2. Schematic diaphragm cell.

differential hydraulic head. The porous diaphragm is used to inhibit the migration of the OH<sup>-</sup> ions from the cathode to the anode; otherwise the mixing of these solutions would result in the formation of hypochlorite instead of the evolution of chlorine.

By maintaining a pH of the anolyte solution of between 3 and 4 and a differential head of five inches between the anolyte and catholyte solution levels, the operation of the cell can be kept in chemical equilibrium to produce a 97 percent chlorine gas at the anode, an almost 100 percent hydrogen gas at the cathode, and an 11 to 12 percent NaOH content in the catholyte effluent, which is replaced by purified brine at 60 to 70°C at the inlet.<sup>4</sup> The diaphragm is usually made by introducing an asbestos slurry into the brine and drawing a vacuum on the inside of the cathode compartment. This deposits the asbestos slurry on the perforated steel screens that serve as the cathode. In time this diaphragm material becomes clogged with impurities and must be removed and replaced.

Fig. 1-3 illustrates the flow sheet of a typical modern chloralkali plant producing chlorine by electrolysis in a diaphragm cell.

The ingredients required are brine, water, and electric power. Brine is made available in one of two ways: (1) Rock salt is delivered to the plant and dissolved in water, or (2) the plant may be located adjacent to underground deposits of salt from which the brine is produced by water injection into a well. Impurities such as the calcium and magnesium ions of the sulfates and chlorides must be removed from the brine solution. This is accomplished by the addition of sodium carbonate and sodium hydroxide in a carefully controlled treatment process followed by sedimentation and filtration. The salt content of this brine must be increased to the optimum level of approximately 26.6 percent (322 g/l) of NaCl at 70°C. This is accomplished by heating the brine and saturating it with purified salt. The latter is obtained from the evaporation step in the processing of the cell liquor.

The water supply used for dissolving the salt should be completely softened for the removal of Ca, Mg, and Fe ions to minimize blockage in the cell diaphragm. This water should also be free of any ammonia ion to minimize the nitrogen content. This reduces the hazard of forming the potentially explosive nitrogen trichloride in the production of chlorine.

The power requirement is approximately 3000 kwh per short ton of chlorine. This is usually a high-voltage AC source, so that it must be put through various pieces of switch gear to step down the voltage and rectify it to DC. Power to the cells is low voltage (4 to 5 V DC) and, depending upon the size and particular design of the cell, the current consumption ranges between 10,000 and 50,000 amp for modern installations.<sup>4</sup>

The products of this electrolysis process are chlorine gas, hydrogen gas (both of which are saturated with water vapor), and the spent cell liquor (caustic).

The gas leaving the cathode is about 99.8 percent hydrogen. It is scrubbed with water both to cool and to remove any traces of salt or caustic, and it is then compressed for supplying various processes or is used as fuel.

The gas leaving the anode is about 97.5 percent chlorine. The remainder usually

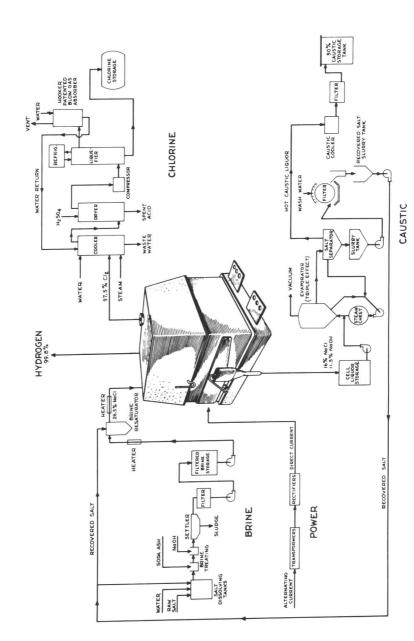


Fig. 1-3. Chlorine-caustic soda plant. Courtesy Hooker Chemical Company.

consists of a mixture of water vapor, oxygen, nitrogen, and carbon dioxide. At this point the gas is hot (210°F), moist, and extremely corrosive. It must be cooled and dried. Oddly enough, it is usually cooled by direct contact with water in a packed tower and then dried by scrubbing with sulfuric acid. The dried chlorine is then compressed to about 60 psi. After compression, it is fed into a special fractionating tower<sup>6</sup> to remove the impurities such as chloroform and chlorinated hydrocarbons. This innovation was introduced about 1930 in an effort to clean the chlorine so that it could be more easily handled by conventional chlorination equipment used for water and waste treatment. The impurities are removed at the bottom of the tower as a solution containing little or no chlorine. Usually these impurities are less than 0.2 percent by weight in liquid chlorine that has not been so treated.

After leaving the fractionating tower, the chlorine gas is then liquefied by refrigeration and pumped to storage tanks, from which it is then pumped into tank cars and ton containers. The trend today is for the manufacturer to ship liquid chlorine in tank cars to packagers, who use the cars as storage from which to fill 150-lb and ton cylinders, which are then shipped directly to the consumer. Each distributor has a liquid bleach manufacturing operation in order to utilize the "snift gas" that would otherwise be wasted in the cylinder-filling operation.

Manufacturing plants also have the problem of recovering the snift or blow gas as well as the chlorine lost in the water used for cooling the gas. Recovery of chlorine from these two waste sources is usually accomplished by some patented process. The Hooker process uses water to absorb the chlorine in the snift gas. This water is then used in the cooler. Upon leaving the cooler, it is heated with steam and then acidified, thus stripping the water of chlorine, which is then put back into the packaging cycle. The Diamond-Alkali process uses carbon tetrachloride to absorb chlorine; the carbon tetrachloride is then heated and stripped of chlorine.<sup>4</sup>

The spent liquor from the cells usually contains about 11.5 percent NaOH and 16 percent NaCl. Before this can be marketed, the salt must be removed and the concentration of caustic must be raised to the optimum 50 percent. To raise to this concentration, the liquid is first passed through a double- or triple-effect evaporator. As it proceeds through the evaporation cycle, the NaOH concentration increases and the salt crystallizes and is separated from the caustic liquor by decantation and filtration. The salt is then washed free of caustic, dissolved, and recycled through the brine system. More salt is removed from the 50 percent caustic by cooling and settling.

Table 1-1 gives operating data on the two leading diaphragm cells now in use.

According to Faraday's laws, one coulomb of electricity deposits exactly 0.00111801 g of silver; or, said another way, a current of one amp deposits 0.00111801 g of silver in one second. According to the second law, the quantity of electricity which liberates one g equivalent weight of an element is the same for all elements. Since the equivalent weight of silver is 107.880, this quantity must be:

$$\frac{107.880}{0.00111801} = 96,493 \text{ coulomb} \tag{1-8}$$

TABLE 1-1 Typical Operating Data for Diaphragm Cells	TABLE 1-1	Typical	Operating	Data fo	or Diaphragm	Cells'
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	Hooker Type S-3C	Diamond Alkali Type D-3
Current (amp)	30,000	30,000
Current efficiency (%)	96.0	96.5
Voltage per cell (average)	3.95	3.82
Power, DC (kwh/short ton Cl <sub>2</sub> )	2820	2720
Cl <sub>2</sub> production (lb/day/cell)	2016	2020
NaOH production (lb/day/cell)	2274	2280
Salt/caustic ratio		
(lb NaCl/lb NaOH)	1.4	
NaOH in cell liquor (%)	11.6	10.5
NaOH in cell liquor (g/1)	146	
Temp. catholyte (°C)	99.5	196°F
H <sub>2</sub> production (lb/day/cell)	59.1	
H <sub>2</sub> cu ft/day/cell at 760 mm 0°C	10,530	
Pounds graphite/short ton Cl <sub>2</sub>	5.3	7.5
Anode life (days)	280	230
Diaphragm life (days)	100-140	115

Typical analyses: Chlorine 97.5%, 0.2 to 0.4% H<sub>2</sub>, 1% CO<sub>2</sub> 0.5% O<sub>2</sub> by vol Hydrogen 99.8-99.9% by vol Caustic 0.1 part NaClO<sub>3</sub>/100 parts NaOH Brine feed 26.6% NaCl, 322 g/l NaCl 65-75° C

Therefore, from Faraday's law we know that 96,493 coulomb (1 faraday) will liberate 1.0080 g of hydrogen and 35.457 g of chlorine in the electrolysis of salt. Converting this to amperes required per pound of chlorine per day, we get:

$$\frac{\text{Amp x 86400 sec/day}}{96,493 \text{ coulomb}} \times \frac{35.457 \text{ g Cl}_2}{454 \text{ g/lb}}$$
 (1-9)

 $\therefore$  Amp x 0.07 = lb/day Cl<sub>2</sub>

Referring now to Table 1-1, we see that 30,000 amp with a current efficiency of 96.0 percent will produce 2016 lb chlorine per day.

*Check*:  $30,000 \times 0.07 \times 96.0\% = 2,016$ 

Electrolysis of Brines in Mercury Cells The method of producing chlorine and caustic utilizing a mercury cathode was discovered simultaneously by two men on different continents. Each was unaware of the other's efforts. One was an American, Hamilton Y. Castner; the other an Austrian, Karl Kellner. Both applied for a patent in 1892.

The first Castner cell installation (a demonstration plant for Mathieson Chemical Company, at Saltville, Virginia, in 1897, designed for 550 amp operation), was later moved to Niagara Falls, New York, where it was operated successfully until 1960. At that time it was replaced by the E.11, the latest version of the Olin-Mathieson mercury cells, with a capacity of 100,000 amp.<sup>4</sup>

The mercury cell has two essential parts: (1) the electrolyzer, and (2) the amalgam decomposer. In the electrolyzer, a salt solution is electrolyzed, making use of a graphite anode and a flowing mercury cathode. Chlorine gas is liberated at the anode, and sodium is deposited at the surface of the flowing mercury cathode, in which it dissolves to form a liquid amalgam. This amalgam flows into the decomposer, where it is decomposed with water to form sodium hydroxide and hydrogen gas. (See Fig. 1-4.)

The principal reactions are as follows:

- 1. Electrolyzer
  - a. At the anode

$$C1^- = \frac{1}{2}C1_2 + e^-$$
 (1-10)

b. At the cathode

$$Na^+ + (Hg)^+ + e^- = Na(Hg)$$
 (1-11)

overall reaction:

NaCl + (Hg) 
$$\xrightarrow{1 \text{ faraday}}$$
 Na(Hg) +  $\frac{1}{2}$ Cl<sub>2</sub> (1-12)

- 2. Decomposer
  - a. At the anode

$$Na(Hg) = Na^+ + (Hg) + e^-$$
 (1-13)

b. At the cathode

$$H_2O + e^- = OH^- + \frac{1}{2}H_2$$
 (1-14)

overall:

$$Na(Hg) + H_2O \xrightarrow{1 \text{ faraday}} NaOH + \frac{1}{2}H_2 + (Hg)$$
 (1-15)

The fundamental differences between this and the diaphragm cell are as follows: The spent brine or anolyte is withdrawn separately from the mercury amalgam. The caustic is produced in the decomposer as a by-product resulting from the preparation of the amalgam to be returned as the mercury cathode. The amalgam is the catholyte and does not mix with the anolyte.

The net result is essentially the same with mercury cells. The ingredients are the same, except for the inventory of mercury required. Both processes use about 1.7 tons of salt per ton of chlorine produced.

Electrolyzer. The purified, saturated (305 g/l) alkaline brine solution is fed to the electrolyzer portion of the cells when the pH is adjusted to a range of 2.5 to 5 with HCl. This is somewhat dependent on the  $CaSO_4$  that can be tolerated in the brine. The pressure on the anode side is kept at atmospheric  $\pm 15$  mm Hg. The direct current in the specified amount of the cell rating (Olin-Mathieson E-11 is 100,000 amp) is applied at a voltage of 4 to 4.5 V between graphite anode and mercury cathode, with the chlorine being liberated at the anode. The spent brine is